

HUBBERT'S PEAK : THE IMPENDING WORLD OIL SHORTAGE

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Invited Presidential Event Presentation

World oil production will peak on Thanksgiving Day, 2005, with an uncertainty of only a month or two. In 1956, M. King Hubbert predicted that U.S. oil production would peak in the early 1970's. Although Hubbert was widely criticized by some oil experts and economists, 1970 was the largest year of U.S. oil production. Hubbert's methods applied to world oil production, show that growth in production has ceased and a decline will follow. The present chaos in energy prices may, in fact, be the leading edge of a major crisis. This means that we must turn to long-term solutions to our future energy problems.

OUR ENERGY CHALLENGE

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Somehow within the next few decades we must find a new energy source that can provide at least 10 terawatts (TW) of clean power on sustainable basis, and do this cheaply. To do this with nuclear fission would require 10,000 breeder reactors. In order for the billions of people in the developing world to achieve and sustain a modern lifestyle, we really need 50 TW. Assuming we don't get it all from "clean coal" or nuclear fission, where is that 10-50 TW of new power going to come from? How will we transport this energy, store it, and transform it? Who will make the necessary scientific and engineering breakthroughs? Can it be cheap enough to bring 10 billion people to a reasonable standard of living? Can it be done soon enough to avoid the hard economic times, terrorism, war and human suffering that will otherwise occur as we fight over the dwindling oil and gas reserves on the planet? Energy may very well be the single most critical challenge facing humanity in this century.

THE ROLE OF CHEMISTRY IN PROVIDING FUELS FOR THE FUTURE

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This presentation will focus on the role that chemistry will play in meeting the challenges for developing fuels for the future. While humankind has tapped into solar, wind, biomass, and geothermal energy sources for millennia, science and technology are the keys for making these sources a significant part of the rapidly growing energy needs of the world in the 21st century. Through the application of chemistry, in concert with physics, biology, biotechnology, nanoscience, engineering, and other disciplines, come clean transportation fuels from biomass, new ways to produce electricity from sun, wind, and the heat of the earth, and hydrogen as a means to provide fuel for transportation, distributed electricity generation, and heating buildings. The presentation will focus on fuels for the future and will address the following questions. What current chemical sciences will initiate the shift to our future fuels? What are some examples of how chemistry today is helping to mold the fuels of the future? Are there gaps in our knowledge of chemistry that need to be filled? What will chemical fuel sciences look like in the future?

FUELS FOR THE FUTURE: THE GLOBAL PERSPECTIVE

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Clearly there are significant differences among the worlds regions and nations regarding needs and issues surrounding development of fuels for the future. For example, technologically advanced nations will strive to secure their supply of fuels to ensure continued prosperity, while developing countries will struggle to develop fuel supplies and infrastructure in order to simply improve their economies and the quality of life of their citizens. This paper will present the global perspective on fuels for the future and address the following global energy issues. How will other nations and regions of the world handle issues such as balancing fuel resource development with environmental stewardship and economic issues? What technologies are other nations considering for future fuel supplies? What role will America play in the world context?

Meeting the Fuels and Energy Policy Challenge

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The attacks of September 11th, the California energy crisis, growing concern over global climate change, and the tremendous progress in new clean energy technologies all suggest a rapidly changing landscape of energy needs, vulnerabilities, and opportunities. The National Commission on Energy Policy intends to propose a series of near-term measures that are necessary to improve our nation's long-range energy position. These recommendations will be contained in the final report of the Commission scheduled for release in late 2004 / early 2005. This presentation will touch on a number of issues under active consideration by the Commission, such as how to harness market forces towards multiple social ends, what key energy technologies deserve greater public and private investment, and how to ensure adequate future supplies of clean energy given current difficulties in siting new generating facilities, waste storage sites, pipelines and transmission lines.

FOSSIL AND RENEWABLE FUELS CHALLENGES FOR THE 21st CENTURY

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Introduction

In a 1981 issue of *Physics Today*, U-C Berkeley anthropology professor Laura Nader wrote that “The energy problem is not a technological problem. It is a social problem. We must build technologies that recognize human frailty.” (1) This sentiment summarizes quite clearly the multi-faceted problem of planning and building an energy infrastructure that is sustainable in the long term and that accommodates societal, economic and political realities. Our hunger for cost-effective and environmentally friendly energy continues to grow into the 21st century [2]. The U.S. Energy Information Administration has forecast that in the first two decades of the 21st century, energy demand will increase by 60% over the level at the end of the 20th century [3]. Fossil fuels (coal, petroleum and natural gas) have been the major primary energy sources, providing over 85% of the total energy demand, and their role is expected to continue growing due to their inherent cost competitiveness compared to non-fossil energy sources. In Pennsylvania, fossil fuels provide about 76% of total energy needs, with coal accounting for over 50% of the electricity generated [4]. Under this energy scenario, where the elimination of fossil fuels from our energy portfolio would irrefutably lead to an energy famine, the 2001 National Energy Policy (NEP) has reported a fundamental imbalance between energy supply and demand, where, if energy production increases at the same rate as during the last decade, the projected energy needs will be 40% higher than the expected levels of energy production [5]. Accordingly, the NEP proposes to advance new, environmentally friendly technologies to increase energy supplies and encourage cleaner, more efficient energy use. To achieve this goal we need (i) to educate and train a workforce of scientists and engineers at the interface of energy and the environment; (ii) to advance fundamental and practical research to develop the required technologies; and (iii) to create public awareness of energy development and use, including information on energy and a clean environment.

While there is much discussion about transitioning the United States and the world to a “hydrogen economy,” the world will undoubtedly rely on the use of fossil fuels for much of its energy needs for some time to come. What remains for engineers and scientists, particularly fuel chemists, is to envision and design the means of maintaining a portfolio of fuels choices so that fuel flexibility, economic growth and environmental protection can be achieved simultaneously.

In this paper, we review some of the remaining technical challenges regarding fuels for mobile and stationary power sources. We also offer suggestions for research and development strategies to overcome these challenges so that we have sufficient and satisfactory fuels for the future.

Fuel Related R&D Challenges

This section is organized by energy sector, highlighting specific challenges faced within each sector.

Transportation Fuels – Spark Ignition Fuels. The EPA-mandated shift in 2006 to ultra-low-sulfur fuels for on-road vehicles will enable significant enhancements in pollution control

technologies for passenger cars and trucks of all classes [6]. For gasoline-fueled vehicles, whether hybrid electric or conventional, the pressure will be to move beyond the ultra-low emissions vehicle (ULEV) category to the super-ultra-low emissions vehicle (SULEV) and equivalent zero emissions vehicle (EZEV) categories [7]. Spark-ignition direct-injection (SIDI) engine development will continue the push toward maximizing SI engine efficiency and will be made more viable by the potential for sulfur-sensitive NOx control strategies that will be enabled by ultra-low-sulfur fuels. A key challenge in this area is overcoming the coking tendencies of the fuel which can lead to clogged fuel injectors and engine deposits. This is a more critical barrier to SIDI engines than conventional SI engines, due to the need to precisely prepare an ignitable but stratified charge to prevent misfiring and excessive hydrocarbon emissions (8).

To achieve the proposed renewable fuels standard, which may require an average renewable fuels content of 5%, the apparent trend is to ramp up production of fuel-grade ethanol [9]. While this is politically attractive and will provide additional markets for farm products, the yield of renewable energy from ethanol production is poor compared to other renewable fuels. Ethanol provides roughly 1.3 units of renewable energy content for each fossil energy unit consumed in its production [10]. This ratio must be improved to obtain a higher renewable energy content.

Transportation Fuels – Compression Ignition Fuels. The shift in 2006 to ultra-low-sulfur diesel fuel for on-road vehicles [6], combined with the phased requirements to reduce diesel particulate matter (DPM) by more than 90% in 2007 and NOx emissions by more than 90% in 2010 [6], will permit greater dieselization of the vehicle fleet without sacrificing air quality. This trend will permit fuel economy improvements that can enhance energy security and can help cut or stabilize CO₂ emissions. To achieve these stringent emissions regulations, advances in both in-cylinder pollutant control and exhaust aftertreatment will be necessary. The trend toward higher fuel injection pressures, common rail fuel injection, injection rate shaping and exhaust gas recirculation will enhance particulate control, but will make fuel systems more sensitive to injector coking. The enhanced coking witnessed with ultra-low-sulfur diesel will require additive or formulation strategies to mitigate this coking tendency to maintain fuel system performance [11]. So-called “low temperature combustion modes,” wherein combustion takes place under rich conditions or through homogeneous charge compression ignition (HCCI) operation, may also provide combined efficiency enhancements and substantially reduced emissions over traditional compression ignition direct injection (CIDI) [12]. In particular, HCCI engine operation may require an entirely new type of fuel and fuel rating approach. A “good” HCCI fuel is not presently well defined by either the standard octane rating or cetane rating specifications [12,13]. Moreover, there are potentially significant impacts on refinery operations if a unique fuel product stream suited to HCCI engine operation is required to achieve the necessary injection and ignition characteristics, which themselves remain a topic of research. Implementation of diesel particulate filters (DPF) on diesel vehicles can reduce DPM emissions by more than 90%, but may require fuel-borne additives or active control techniques to burn off collected particulates (referred to as trap regeneration) [14]. Control strategies for NOx may be based on adsorber catalysts, which require a brief swing to locally fuel-rich conditions to reduce adsorbed NOx. This may be achieved by fuel injection into the exhaust or mild fuel reforming with a catalytic fuel reformer or by in-cylinder “reforming” from a late fuel injection pulse [15]. In both the DPM and NOx control strategies, there are unresolved issues regarding the interaction of fuel formulation and the effectiveness of the catalytic control technologies.

A nationwide trend in municipal transit has been to convert from diesel to natural gas-fueled buses. While this trend yields immediate benefits for total particulate matter (PM) emissions, there is evidence that PM emissions from natural gas engines without oxidation catalysts are higher and more of a health hazard than those from a diesel engine equipped with a DPF [16]. In addition, natural gas-fueled engines operate at lower efficiency than conventional diesel engines and typically emit high levels of total hydrocarbons, due to unburned methane emissions. Hydrogen enrichment of natural gas has been shown to provide the potential for substantial enhancements in efficiency, reduction in emissions and a practical means of incorporating hydrogen into the existing fuel infrastructure [17]. However, the impacts on durability, operability, safety (particularly with regard to the effectiveness of odorants for leak detection) require further study. In addition, there is a potential for onboard hydrogen generation through incorporation of solid oxide fuel cells as auxiliary power units on transportation vehicles. The uses of this source of hydrogen for enabling low temperature combustion, HCCI and reduced emissions during conventional CIDI operation represent a substantial opportunity for emissions reduction [18].

With regard to renewable fuels for CIDI engines, there has been a recent surge in interest in biodiesel and coordinated efforts by producers, distributors and regulators to achieve viable fuels standards and specifications so that customers and original equipment manufacturers [OEMs] can be confident of the performance and quality of biodiesel. The challenges with biodiesel are many, however, since users may be interested in neat biodiesel ("B100"), the widely used 20 volume % blend ("B20") that the Energy Policy Act of 1992 [EPA] regulations specifically identify as necessary to obtain renewable fuel credits, or a low-level blend for the purpose of providing a lubricity enhancement to the base diesel fuel (e.g., a 2 vol.% blend, "B2"). Fuel system operating parameters such as fuel injection timing, duration and rate may be affected by the changes in fuel density and calorific value at these various biodiesel usage levels [19]. Also, as with the production and distribution of petroleum-derived fuels, there are needs for each stage of the supply chain to adhere to proper fuel processing, handling, and storage practices to ensure reliable performance for the end user. In the case of biodiesel, remaining critical issues involve the widely observed increase in NO_x emissions and the need for robust measures to assess and certify the oxidative stability of the fuel [20]. Also, since there are resource limitations on biodiesel production, a challenge is to find ways to maximize the yield and quality of biodiesel produced from the available agricultural resources [21].

Synthetic diesel fuels, produced from, or containing, components from natural gas, biomass, oil sands and coal, can provide a means of extending and replacing petroleum supplies [22]. For instance, stranded natural gas resources can be converted to high ignition quality, zero-sulfur Fischer-Tropsch [F-T] diesel fuel. However, F-T diesel is widely known to have low lubricity and very high cetane number, greater than 70. The lubricity problem can be overcome with additives, but the cetane number poses a challenge for the refiner. There is no currently realizable benefit from using a neat fuel with a cetane number above 55. However, such fuel streams may provide a cost-effective means of upgrading lower quality middle distillate streams in the refinery to an acceptable cetane number. Biomass-derived F-T diesel, produced from biomass gasification, has the potential to supply substantial high-quality diesel fuel with very high renewable energy to fossil energy ratio, but faces challenges associated with biomass gasification and producing a synthesis gas of sufficient quality for the F-T process [10]. When derived from coal co-processing rather than from indirect liquefaction or from the hydroprocessing of oil sands, synthetic fuel

stocks may have adverse impacts on diesel fuel quality, such as enhanced sooting tendency and reduced ignition quality [23].

Stationary Power Generation – Carbon Dioxide Emissions.

The current fossil energy scenario is undergoing significant transformations, especially to accommodate increasingly stringent environmental challenges of contaminants such as sulfur dioxide, nitrogen oxides and mercury, while remaining affordable. Furthermore, fossil fuel utilization is inherently associated with greenhouse gas emissions, especially carbon dioxide. Pennsylvania is the tenth largest producer of carbon dioxide in the U.S. from electric utilities, with over 2,700 thousand short tons/square mile [24]. Should worldwide government policies dictate a reduction in greenhouse gas emissions or the imposition of carbon taxes, fossil fuels would lose much of their competitive appeal to nuclear and renewable energy sources. However, the current non-fossil fuel energy share of the worldwide energy market is below 15% (and below 2.5% in Pennsylvania), and therefore it is more likely that fossil fuel energy producers would adapt to the new requirements by developing and implementing emission control and trading strategies.

Research Recommendations for Fuels for the Future

This section is organized by energy sector, highlighting specific recommendations for research to address the challenges that have been identified. With regard to carbon sequestration, a series of carbon sequestration research programs is presented, including carbon storage by mineral carbonates, geological sequestration and capture systems

Transportation Fuels. *1. Fuel Stability* Research is needed in the areas of oxidative and pyrolytic stability of automotive fuels, particularly in: the coking tendency of gasolines for SIDI engines and ultra-low-sulfur diesel fuels; and the oxidative stability of biodiesel.

2. Fuel for Advanced Combustion Regimes Additional research is needed in fuels for HCCI applications, since both the fuels and the engines themselves are under development, particularly to assess the impacts of producing HCCI fuels on refinery operations.

3. Synthetic and Renewable Fuels Research is needed on engine configuration and operating strategies for capitalizing on the extremely high cetane number available in F-T diesel fuels. Further study is needed on the impacts of using fuels produced from the co-processing of coal and hydroprocessing of oil sands on the combustion and ignition quality of diesel fuels. For renewable fuels, research is needed to maximize the renewable content achieved per unit of fossil energy input, where presently for ethanol the ratio is 1.3 and for biodiesel it is 3. For biodiesel fuels, research is needed to overcome the NO_x emissions increase associated with biodiesel use.

Stationary Power Generation – Carbon Sequestration.

1. Mineral carbonation, which includes the reaction of magnesium-rich minerals with CO₂ to form stable mineral carbonates, is a novel and promising approach to carbon sequestration. Suitable feedstocks include olivine (Mg₂SiO₄) and serpentine (Mg₃Si₂O₅(OH)₄) minerals, although serpentine exists in far greater quantities. The mineral carbonation approach offers several inherent advantages: long term stability of benign mineral carbonates; the vast capacity of natural mineral deposits; and the overall process being exothermic, and therefore potentially economically viable (25). However, the reaction kinetics are a substantial drawback. Previous studies have required extensive comminution of the raw minerals (<37 µm), heat treatment (600-650°C), high temperatures (>155°C), high partial pressures (>125 atm), and long reaction times (>6 hours) to overcome the kinetic barriers.

The primary research objective should be to investigate the effectiveness of various pretreatment methods aimed at promoting and accelerating carbonation reaction rates and efficiencies through surface activation and moisture removal. Previous studies have

shown that mineral dissolution rates are surface controlled, and the carbonation reaction stops when the magnesium at the mineral's surface becomes depleted and/or blocked due to mass transfer resistance. It has also been demonstrated that the inherent water content of serpentine is detrimental to the carbonation process. Therefore, it can be envisioned that an increase in surface area and decrease in moisture would result in higher reaction rates and efficiencies. This would allow the integration of various synergistic features for the development of a cost-effective sequestration technology, including accelerating the carbonation efficiency without extensive mineral particle comminution or heat treatment and lowering the temperature and pressure conditions of the carbonation reactions.

The most promising results have been with chemically activated serpentines. A carbonation efficiency of nearly 53% was observed at 20°C, and relatively low pressure, 45 atm. These reaction conditions are a significant improvement over previous studies involving thermal activation and grinding that have required temperatures over 155°C and pressures of at least 125 atm (26). Furthermore, high-temperature heat treatment was avoided and a coarser particle size, 75 μm , was used in this work, compared to <37 μm in previous studies. Current work is focused on the development of a continuous CO₂ sequestration module.

2. Geologic Sequestration. The existence of large volumes of accessible subsurface brine provides a potential high capacity route for the conversion of CO₂ into geologically stable mineral carbonates, such as calcium carbonate and magnesium carbonate (27). Under the appropriate conditions, CO₂ dissolves in brine to initiate a series of reactions that ultimately leads to the bonding of carbonate anions to various metal cations inherent in brine to precipitate carbonates. Subsurface saline aquifers may sequester CO₂ in various forms. However, any ex-situ sequestration process will have to rely on an efficient conversion to mineral carbonates. An investigation into the parameters, most importantly pH, that affect this conversion rate is required, since the evolution of brine pH following adjustment and during reaction with CO₂ at various temperatures and pressures is highly variable.

The rate of the mineral trapping process is slow and serves as the major disadvantage of this technology. It has been suggested that pH has a significant effect on both conversion rate and the specific species that are precipitated (28). The conversion to carbonates can thus be promoted by increasing brine pH through the addition of a strong base. This research qualitatively identifies the effects of various parameters on carbonate precipitation. However, pH evolution throughout the reaction is not well documented. It is necessary to further understand the effects of temperature, pressure, and most importantly pH on the formation of mineral carbonates during the reaction of CO₂ with various natural gas well brines (29). Additionally, the evolution of brine pH following a pH adjustment, but prior to reaction with CO₂, should be studied. This analysis would help determine a relationship between brine composition and a brine's ability to maintain an elevated pH over time.

Preliminary results have revealed large differences in the metal concentrations of brines from various depths and locations. These compositional differences are related to the brine's ability to maintain an elevated pH after treatment with a strong base to address the natural acidity of brine (29).

3. Capture. The costs of current CO₂ separation and capture technologies are estimated to be about 75% of the total cost of ocean or geological sequestration, including the costs for compression to the required pressure for subsequent sequestration (30). New solid-based sorbents should be investigated, where amine groups would bond to a solid surface, resulting in an easier regeneration than with conventional liquid-phase amine absorbents (31). The supports used

thus far, including commercial molecular sieves, are generally expensive and hinder the economical viability of the process. Accordingly, there is a need to find low-cost precursors that can compete with expensive commercial supports, and to develop effective solid sorbents that can be easily regenerated, and therefore, which would have an overall lower cost over their lifetime.

Activated carbons are sorbents used in a wide range of household, medical, industrial, military and scientific applications, including gas-phase and liquid-phase processes. The activation process, together with the intrinsic nature of the precursors, strongly determines the characteristics of the resulting activated carbons. Many precursors have the inherent chemical properties, fine structure and relatively low price that make them excellent raw materials for the production of activated carbons. It is anticipated that high-surface-area carbon materials that have been amine impregnated would satisfy this need and provide a superior low-cost CO₂ sorbent (32).

Conclusions

Energy security and development of a sustainable energy infrastructure require advancements in our understanding of the production and utilization of energy resources and of mitigation of their environmental impacts. Such understanding can only come from targeted, fundamental research. It is incumbent on government, industry and academia to invest in frank discussion and insightful planning to ensure that we develop this understanding. Further, it is important to recognize that the nation needs a balanced energy portfolio, rather than relying so heavily ($\geq 99\%$) on petroleum for our transportation fuels. All energy resources have inherent technological advantages and disadvantages; all have economic incentives and disincentives; and all have associated environmental issues. Our challenge is to strike the appropriate balance among all these factors.

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COAL-DERIVED LIQUID FUELS: AN OPTION TO HELP MEET A GROWING DEMAND

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Introduction

The events of September 11, 2001 have heightened U.S. awareness of the need for greater national security in all aspects of our daily lives. Energy is the key component for the continued operation of a modern society and security of supply is crucial for our continued economic and social prosperity. Every day the U.S. imports a substantial quantity of petroleum (53 percent in 2002) and a substantial quantity of this comes from politically unstable areas of the world. For example, the U.S. imports about 2.5 million barrels per day of petroleum crude and refined products from the Middle East.

Energy security will require not only political, but technological approaches to insure a continued secure supply of affordable transportation fuels. Transportation is the focus because almost all of our transportation energy is derived from petroleum. Although diversity of petroleum supply is important, only energy produced from our domestic resources will truly be secure. These domestic resources include renewables, petroleum, natural gas and our vast coal resources that can provide electricity, hydrogen and liquid fuels to meet our stationary and mobile energy demands. Thus, there are many choices that can be made regarding energy source and fuel to reduce our dependence on imported oil. This paper addresses one combination – the conversion of coal to zero sulfur, high performance Fischer-Tropsch fuel that is compatible with our present liquid fuel infrastructure and can be used directly or reformed at distributed locations to produce hydrogen.

The Polygeneration Concept

It is envisioned that production of these F-T fuels will follow a progression based on Integrated Gasification Combined-Cycle (IGCC) technologies. After successful demonstration, “polygeneration” plants that produce liquid fuels and electric power are likely to be deployed. The plants would be designed to incorporate carbon capture with appropriate storage in oil reservoirs for enhanced oil recovery or in saline aquifers.

In its simplest form the polygeneration concept consists of diverting clean coal-derived synthesis gas from the combined-cycle-power block of an Integrated Coal Gasification Combined Cycle (IGCC) unit to a synthesis reactor. This plant could also be designed to divert some of the hydrogen produced for use in fuel cell applications.(Figure 1). The tail gas from the synthesis reactor consisting of unreacted synthesis gas, carbon dioxide, water, and light hydrocarbons is then combusted in the combined-cycle power generation unit. Combining processes in this manner has certain technical and economic advantages. Coal cannot be combusted directly in gas turbines; it must first be converted into clean synthesis gas. Once the coal is in gaseous form, the high efficiencies associated with gas turbine combined cycle performance now become accessible to coal. However, once the clean synthesis gas has been produced from the coal, the plant can be made even more efficient by co-producing liquid transportation fuels through Fischer-Tropsch (F-T) or other synthesis technology. Compared to a stand-alone F-T facility, using a once through synthesis process in this configuration avoids the significant inefficiencies of synthesis gas

recycle and light hydrocarbon reforming that would be necessary in configurations that produce only an all-liquid product

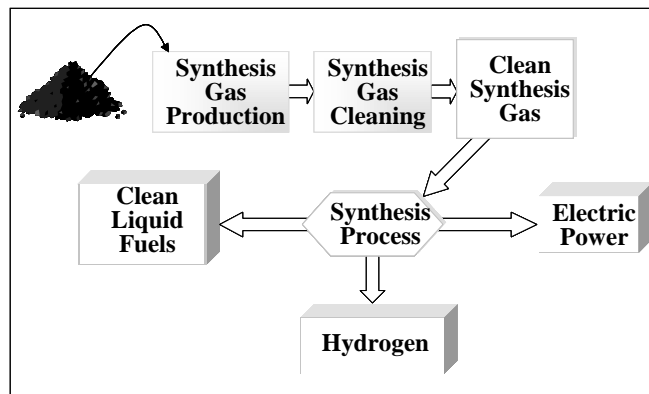


Figure 1. The Overall Technology Concept

The basic IGCC plant needs to be modified to reconfigure it as a polygeneration facility. The additional equipment required includes synthesis, product recovery and refining, water-gas shift, hydrogen recovery, sulfur polishing for synthesis gas cleaning, and product tankage and shipping facilities. In addition to this equipment, it is necessary to modify the steam system of the combined cycle section since the synthesis and shift reactors produce steam that is used to supplement the steam cycle of the combined cycle electric power generation system.

Technology Status

The chemistry is proven, essentially two major exothermic reactions are involved – the reaction of carbon monoxide with hydrogen, followed by carbon monoxide and water reacting through the water-gas shift. At end of WWII, F-T was being studied by most industrial nations, but the low cost and high availability of oil led to decline in interest. The only commercial plants using this technology today are in South Africa (Sasol) and Malaysia (Shell). At the present time, no coal-based facilities based on modern entrained gasification have been constructed that can produce both liquid transportation fuels and electric power., although a project team led by Waste Management Processors, Inc. has been selected by the Department of Energy to build a pre-commercial scale plant in the eastern Pennsylvania anthracite region. This plant would polygenerate 5,000 barrels/day F-T fuel, 50 MWe net electricity and some low pressure steam for industrial heating.

In order to improve the current technology and achieve the increases in performance and reduction in costs, enabling R&D is necessary in the following broad areas:

- Synthesis gas generation (Gasification)
- Gas cleaning
- Synthesis gas conversion reactors, catalysts, catalyst/wax separation
- Integration of power production with synthesis gas conversion
- Carbon capture and sequestration
- Hydrogen separation
- Systems analyses to optimize the plant efficiency, operability, safety and economics

COAL AS RESOURCE FOR FUELS OF THE FUTURE

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Introduction

Oil is a finite resource and there is credible and increasing evidence to suggest that world oil production could peak and start to irreversibly decline within a decade or two. Some analysts even expect peak oil production to occur as soon as 2007. Abundant, low cost liquid hydrocarbon fuels that power automobiles, trucks, aircraft, trains, ships, and the military are the lifeblood of modern economic societies. There are no obvious alternatives to these liquid fuels envisioned for several decades. The peaking of world oil production, resulting in an irreversible decline in petroleum production and an imbalance between supply and demand, will dramatically increase oil prices and have severe long-term economic impacts both nationally and internationally unless decisive actions are taken.

The key question is how can the U.S. be prepared for this inevitable peak and decline in future world oil production? The long-term solution is to move completely away from a petroleum-based transportation system towards development of a more sustainable energy structure. Several options have been proposed for future clean transportation energy systems. The "Hydrogen Economy" and "electrification" are two of the most prominent suggestions. In both of these systems, primary energy sources are required to produce the energy carrier, be it hydrogen or electricity. These primary energy sources could be renewables, nuclear or fossil fuels. If fossil fuels were to be used, carbon dioxide capture and sequestration technologies might be necessary to limit greenhouse gas emissions.

Utilization of these future energy carriers in our transportation sector will require moderate to complete changes in the current transportation fuels infrastructure. Electric transportation will require significant breakthroughs in low cost, high power density electric storage battery technology and even when battery technology has improved, changing from the current petroleum based transportation infrastructure to an electric based system could take several decades. Transitioning from liquid petroleum to gaseous hydrogen will require a complete change in the current liquid fuels production, distribution, and end-use infrastructure. A change of this magnitude is likely to take many decades and billions of dollars to accomplish. The transition, of course, will be gradual and the actual time required to accomplish it is uncertain. Much depends on success in overcoming the major hurdles that this transition poses. These include obtaining breakthroughs in reliable and economically competitive fuel cell vehicle technology and hydrogen on-board storage. Also, large numbers of new central and distributed hydrogen production facilities will need to be constructed together with an extensive new pipeline delivery network and new dispensing facilities. The current Bush administration has already endorsed the concept of a future hydrogen economy and has proposed several government/industry programs including the FreedomCar and FutureGen initiatives. The goal of the Department of Energy is to speed the transition to a hydrogen economy and the hope is that the necessary technologies and infrastructure will be in place for major implementation of hydrogen by 2035. The National Academies in their study "The Hydrogen Economy: Opportunities, Costs Barriers and R&D Needs" supports the movement toward a hydrogen

economy but also cautions that this fast tracking requires major breakthroughs and cost reductions that may delay a complete infrastructure change until 2050 or later. The Academy states, "Widespread success is not certain", and further recommends that DOE should "keep a balanced portfolio of R&D efforts and continue to explore supply-and-demand alternatives that do not depend upon hydrogen."

It is clear, therefore, that the sustainable hydrogen energy solution is a long-term option where hydrogen, produced eventually from sustainable energy sources such as renewables and nuclear, is used in many energy sectors including transportation. Hydrogen has many potential advantages. It would eventually replace petroleum, which will be necessary once oil production has peaked and is in decline. It could essentially eliminate carbon dioxide emissions, reduce urban and regional pollution, and may provide a sustainable and affordable energy source for the future. As the National Academy cautions, if we embarked on this hydrogen transition today, as a high national priority, it is unlikely that a complete infrastructure change could be accomplished much before 2040. But with the threat of world oil peaking looming, 2040 may be too late to complete the transition to a hydrogen energy system and avoid an economic crisis.

If proactive action is taken to address future energy supply and demand, there are three approaches and all three must be addressed simultaneously: increase end use efficiency, diversify liquid fuels supply, and prepare for a long term non-petroleum-based economy like hydrogen or electricity. Reducing petroleum consumption can be accomplished by demand side management. This means implementing more stringent CAFÉ standards to improve fleet efficiency and encouraging deployment of hybrid electric vehicles. However, conservation alone is not a quick fix. It will take almost two decades before the benefits of improved end-use efficiency have major national impact. The supply side preparedness options are to supplement declining petroleum fuels with liquid hydrocarbon fuels from our non-petroleum domestic resources in the mid term and, in the long term, to eventually replace liquid fuels with hydrogen or electric power obtained from renewable resources.

If liquid hydrocarbon fuels are to be produced from our non-petroleum domestic energy resources then the choices are biomass, natural gas, shale oil, or coal. Although several domestic resources will be required in a balanced energy portfolio, there are limits to each potential resource. Biomass fuels can make a contribution but will be limited because of huge land use requirements. Domestic natural gas production is in decline and the gas would have to be imported as LNG. There is no commercial technology yet to exploit methane hydrates, although they could be important in the future. Shale oil, while a large domestic resource, lacks commercially viable technology. The most practical supply option is to produce liquids from the nation's coal reserves. Coal, our most abundant domestic fossil resource, with over 250 years supply, could therefore be a practical and major source of clean liquid fuels. This paper discusses the concept of using our vast coal resources to provide liquid hydrocarbon fuels in the mid term and hydrogen in the long term.

Using Coal to Produce Clean Liquid Hydrocarbon Fuels

At the present time *no* coal-based facilities based on modern entrained gasification have been constructed that can produce both liquid transportation fuels and electric power. In the US there are two operational IGCC plants producing only electric power. These are the Polk plant near Tampa, Florida and the Wabash facility in Indiana. The Tampa plant uses the Texaco coal gasification process and the Wabash plant uses the E-Gas process. Both Texaco and E-Gas are modern entrained flow gasifiers.

At Mitretek Systems conceptual commercial plants have been simulated using computer models to estimate the technical performance and economics of coproduction plants. If current technology were used, the required selling price (RSP) of the clean liquid fuels produced would be about \$37/barrel, advanced technology with no carbon sequestration would reduce this cost to about \$31/barrel, and advanced technology with carbon sequestration would require a RSP of about \$40/barrel. On a crude oil equivalent basis these RSPs should be reduced by at least \$5/barrel because these high quality Fischer-Tropsch fuels will have a premium over crude oil of at least \$5/barrel. Therefore the crude oil equivalent RSP for the advanced sequestered plant will be \$35/barrel if the value of the coproduced power were \$36/MWH. If the power value were \$50/MWH, the RSP of the liquid fuels would be reduced to \$30/barrel on an equivalent crude oil basis.

Using Coal to Produce Hydrogen

At Mitretek Systems conceptual commercial plants have also been simulated using computer models to estimate the technical performance and economics of producing hydrogen and electric power from coal. The performance and economics of these technologies are analyzed including configurations for carbon sequestration. For comparison, the economics of producing hydrogen from natural gas has been included.

Hydrogen can be produced from coal with current gasification technology at about 64 percent efficiency (HHV basis) for a cost of production in the range \$6.50 to \$7.00 per MMBtu. The need to sequester carbon dioxide from such a facility would raise this production cost to just over \$8.00/MMBtu and decrease efficiency to about 59 percent. Advanced gasification technology and membrane separation has the potential to reduce the cost of production of hydrogen with carbon sequestration to less than \$6.00/MMBtu and increase the efficiency of production to about 75 percent. However, considerable additional R&D and performance demonstration is necessary to verify this.

If hydrogen is produced in an advanced gasification coproduction facility that also generates electric power the production costs of the coproduced hydrogen can be reduced depending on the value of the power. If the coproduced electric power is valued at \$35.6/MWH (the cost of producing power from a natural gas combined cycle plant (NGCC)) hydrogen can be produced for about \$5.50/MMBtu. If the carbon dioxide is sequestered in this coproduction facility, the cost of hydrogen is only slightly increased if it is assumed that the coproduced power is valued at \$53.6/MWH (the cost of producing power from a sequestered NGCC plant). Utilization of advanced membrane separation technology has the potential to reduce hydrogen production costs to about \$4.00/MMBtu.

The greatest potential for reducing the production cost of hydrogen from coal is in configurations that include solid oxide fuel cells (SOFC). Coproduction facilities that use SOFC topping cycles to produce electric power and hydrogen have the potential to reduce the production cost of hydrogen to below \$4.00 per MMBtu. Clearly such potential warrants continuing RD&D in such integrated facilities that include advanced coal gasification, SOFC topping cycles, and advanced membrane separation technologies. However, it must be cautioned that many of these advanced systems are only in the research phase and significant progress in demonstration and scale up must be made before these systems become a commercial reality.

Costs of producing hydrogen from traditional steam methane reforming of natural gas are of course dependent on fuel costs. If natural gas is \$3.15/MMSCF then the resulting cost of hydrogen is about \$5.50/MMBtu. Eventually sustainable production of hydrogen

from renewable sources like sunlight using photovoltaic (PV) water electrolysis could be a future goal. Continuing RD&D to significantly reduce the costs of PV systems is necessary for hydrogen production costs to be in the same range as production from coal.

Carbon Dioxide Emissions Implications of Using Coal to Produce Clean Fuels and Hydrogen

The carbon dioxide implications of using coal to produce both hydrogen and clean liquid fuels have been analyzed. Plant configurations that capture and sequester the carbon dioxide have been simulated along with plants that do not capture the carbon dioxide and the resulting tailpipe carbon dioxide emissions have been estimated and compared to those from conventional petroleum-based transportation systems. For clean liquid fuels systems, a future sequestered coproduction plant producing transportation fuels used in diesel/hybrid vehicles and electric power will produce only about 0.16 pounds of net carbon dioxide per mile compared to 0.79 pounds of carbon dioxide per mile for a current conventional petroleum-based vehicle.

For coal to hydrogen systems, if the hydrogen produced is used in fuel cell vehicles that obtain 62.5 miles per gallon, even with no carbon capture and sequestration the resulting carbon dioxide emissions would only be about one percent higher than conventional current petroleum based systems.

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CATALYTIC DEHYDROGENATION OF HYDROCARBONS: ALTERNATIVE, ONE STEP PROCESS TO PRODUCE PURE HYDROGEN AND CARBON NANOTUBE BYPRODUCTS

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Introduction

Traditionally, hydrogen has been produced by reforming of natural gas to produce synthesis gas, followed by the water-gas shift reaction to convert CO to CO₂ and produce more hydrogen, followed by separation and purification procedures. In the "FutureGen" concept¹ advocated by the U.S. Department of Energy, the syngas would be produced by coal gasification.

Non-oxidative, catalytic decomposition of hydrocarbons is an alternative, one-step process to produce pure hydrogen. Nanoscale, binary Fe-based alloy catalysts supported on high surface area alumina [(0.5%M-4.5%Fe)/Al₂O₃, M=Mo, Ni or Pd] have been shown to have high activity for the catalytic decomposition of undiluted methane, ethane, or propane into pure hydrogen and multiwalled carbon nanotubes^{2,3,4}. One of the problems with non-oxidative dehydrogenation is coking of the catalyst and reactor due to carbon build up. Under proper reaction conditions, however, these binary catalysts promote the growth of carbon nanotubes that transport carbon away from the catalyst surfaces, thereby preventing catalyst deactivation by coking as well as producing a potentially valuable by-product.

For utilization of fuel cells in vehicles, it is desirable to have a simple process for producing hydrogen from liquid fuels on-board. Therefore, we have also developed catalysts that are very effective for one-step production of pure hydrogen from cyclohexane and methyl cyclohexane⁵.

Experimental Procedures

Detailed descriptions of the experimental procedures have been given elsewhere^{2,4,5,6}. Briefly, the catalysts are prepared by deposition of the metal precursors onto the alumina or stacked-cone CNT by either coprecipitation or incipient wetness procedures using aqueous solutions of the appropriate metal salts. The resulting paste is extruded into pellets that are vacuum-dried and calcined for 5 hours at 500°C. Normally, one gram of catalysts is loaded in the continuous flow reactor and reacted in situ in flowing hydrogen at 700°C for 2 hours prior to reaction. The undiluted hydrocarbons are then fed to the reactor in precisely controlled amounts using mass flow controllers for gaseous alkanes and a syringe pump for liquid hydrocarbons. The products are measured by on-line gas chromatography.

Results and Discussion

Gaseous alkanes. Nanoscale, binary, Fe-M catalysts supported on alumina (0.5%M-4.5%Fe/ γ -Al₂O₃, M = Ni, Mo, or Pd) have been shown to decrease the decomposition temperature of methane, ethane, and propane by 400-500 °C. For methane (Figure 1), the only decomposition products are hydrogen and carbon in the form of multi-walled carbon nanotubes (CNT), while ethane and propane decompose to hydrogen, methane, and CNT. The most active temperature range for all three feed gases is 650-800 °C, where 70-90 % of the product gas is pure hydrogen and the remainder is unreacted methane. In Figure 1, the hydrogen production from methane is shown as a function of temperature for the three binary

catalysts, a 5% Fe/Al₂O₃ catalyst and the alumina support (non-catalytic).

Characterization of the catalysts by XAFS and Mössbauer spectroscopy, TEM, and XRD indicates that the active phase is an Fe-M-C austenitic metal alloy and that the catalyst particles are anchored to the alumina support by an Fe-aluminate, hercynite⁶. The catalysts exhibit good time on stream behavior because the Fe-M-C phases are very effective in stabilizing carbon in the form of CNT, which efficiently carry the carbon away from the active alloy particle surfaces.

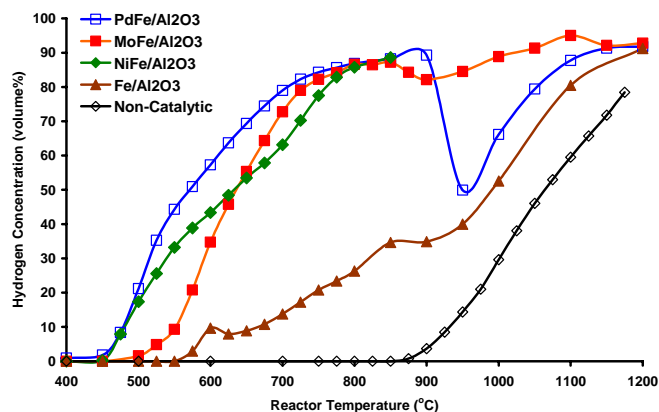


Figure 1. Catalytic decomposition of methane: hydrogen concentration vs. temperature

High resolution TEM has been used to investigate the structures of the CNT. Multi-walled CNT with parallel, concentric, graphene walls are produced at high temperatures (650-700 °C). At low temperatures (450-500 °C), a stacked-cone CNT (SCCNT) structure is produced in which the graphene sheets lie at an angle to the tube axis, which results in extensive graphene sheet edge openings at the circumference of the CNT (Figure 2). Consequently, most of the graphene sheet surface, both exterior and interior, is accessible from the outer periphery of the SC-CNT. Additionally, the outer surface of the SC-CNT has a high density of active carbene sites⁷. Because of this structure, the SC-CNT appear promising as hydrogen storage materials, catalyst supports, and sorbents. Preliminary measurements on hydrogen storage have been conducted by Bockrath and co-workers at the National Energy Technology Laboratory⁸. We have explored the use of SC-CNT as catalyst supports, as discussed further below.

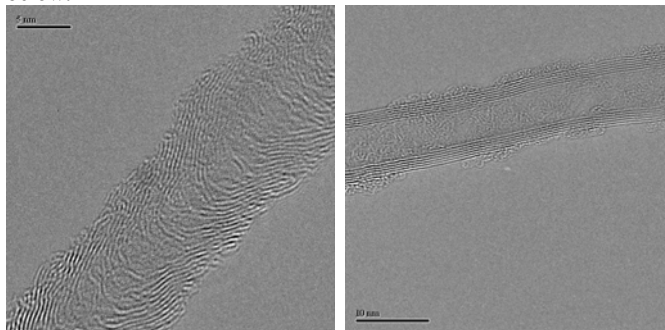


Figure 2. Catalytic decomposition of propane produced stacked-cone CNT at 475 °C and multi-walled CNT with concentric parallel graphene sheets at 625 °C.

Liquid hydrocarbons. In our initial studies of catalytic dehydrogenation of liquid hydrocarbons, we are investigating dehydrogenation of the model compounds cyclohexane and methyl cyclohexane. Cyclohexane is completely converted to benzene and hydrogen at 315 °C using a catalyst consisting of only 0.25 wt.% Pt supported on stacked-cone CNT (Figure 3). Similar results were obtained for the catalytic dehydrogenation of methyl cyclohexane to toluene and hydrogen. Additional studies are planned using several alloy catalysts and other hydrocarbon liquids, including Fischer-Tropsch fuels.

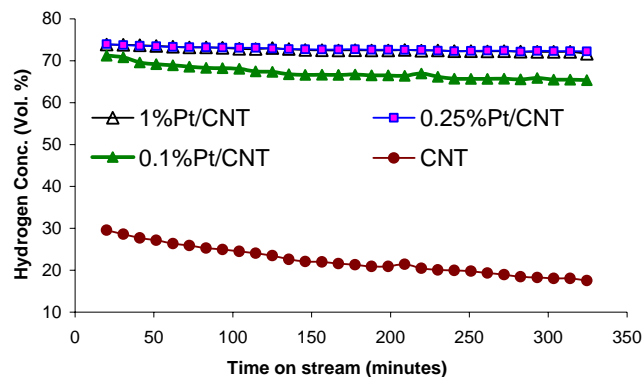


Figure 3. Hydrogen production by catalytic dehydrogenation of cyclohexane using Pt on SC-CNT catalysts. The results obtained using the SC-CNT alone are also shown.

Future work

Topics to be investigated in future research are briefly summarized below.

1. Development of a fluid bed process for continuous production of hydrogen and carbon nanotubes by catalytic dehydrogenation of gaseous alkanes.
2. Further investigation of applications for stacked-cone CNT, including gas storage, catalyst supports, and as environmental sorbents.
3. Development of more economical alloy catalysts for dehydrogenation of hydrocarbon liquids.
4. Catalytic dehydrogenation of additional hydrocarbon liquids, including Fischer-Tropsch fuels.
5. Carry out an economic and energy balance analysis of catalytic dehydrogenation of gaseous and liquid hydrocarbon fuels.

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TRANSPORTATION FUELS AND DOE'S VISION OF THE FUTURE

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Introduction

The Department of Energy's end-use transportation fuels research is coordinated by the Fuels Technologies Sub-Program within the FreedomCAR and Vehicle Technologies Program in the Office of Energy Efficiency and Renewable Energy, and is designed to support the major R&D programs in transportation research including the Freedom CAR Initiative and the 21st century Truck Partnership (1). The Fuels Technologies sub-program has three component activities as shown in Figure 1:

- Advanced Petroleum-Based Fuels (APBF)
- Non-Petroleum-Based Fuels (NPBF)
- New Technology Impacts

APBF and NPBF activities are undertaken to enable current and emerging advanced combustion engines and emission control systems to be as efficient as possible while meeting future emission standards and to reduce reliance on petroleum-based fuels. To differentiate these two activities, an advanced petroleum based fuel consists of a petroleum base fuel derived from crude oil, possibly blended with performance-enhancing non-petroleum components. In contrast, a non-petroleum based fuel is envisioned as consisting of a fuel or fuel-blending component derived primarily from non-crude-oil sources such as agricultural products, biomass, natural gas, or coal.

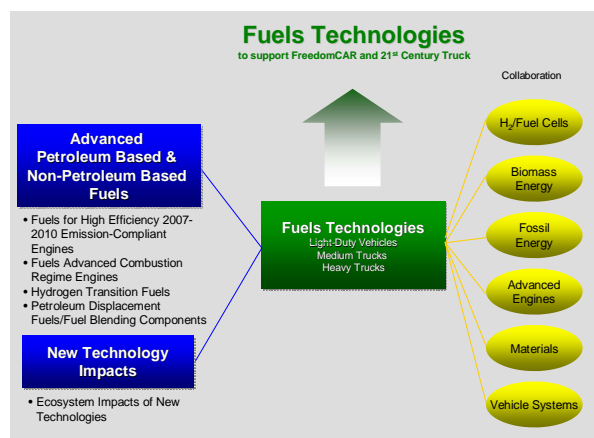


Figure 1. Activities, Collaborations, and Outputs of the Fuels Technologies Sub-Program

A major focus of both the APBF and NPBF activities is to determine the impacts of fuel properties on the efficiency, performance, and emissions of advanced internal combustion engines. For the long term, the Fuels Technologies sub-program is focused on fuels optimized for advanced combustion regimes, a general term intended to include a variety of in-cylinder strategies that have the potential to provide diesel-like or greater efficiency with extremely low engine-out emissions. Homogeneous charge

compression ignition (HCCI) and low-temperature combustion (LTC) are examples of such combustion regimes. Research will be conducted to identify fuel-related factors which can foster the expansion of HCCI and LTC operability. Co-development of fuels and engines is likely to be a necessary step in the post-2010 timeframe due to increasingly strict emissions regulations. This strategic approach of co-development necessitates a much-improved state of fundamental knowledge about fuel composition and properties, and their impact on engine combustion phenomena. Additionally, the NPBF activity (Figure 2) has the goal of identifying practical, economic fuels and fuel-blending components which have the potential to directly displace significant amounts of petroleum. These fuels and fuel components are anticipated to be derived from non-fossil sources such as biomass, vegetable oils, and waste animal fats, as well as from fossil sources other than light, sweet crude oil such as natural gas, heavy crude, oil sands, oil shale, and coal. The production of diesel fuel from these sources is technically feasible and some are coming into limited use in the US. The NPBF activity focuses on the properties and quality of the finished fuels derived from these sources and not primarily on their production.

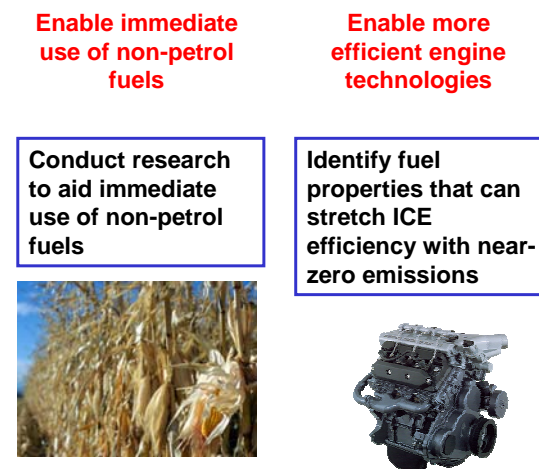


Figure 2. NPBF aims to replace petroleum-based fuels and enable more efficient engine technologies

Specific Program Goals of the Fuels Technology activity relative to reducing the US dependence on petroleum include:

- By 2007, identify fuel formulations optimized for use in 2007-2010 technology diesel engines that incorporate use of non-petroleum-based blending components with the potential to achieve at least a 5 percent replacement of petroleum fuels.
- By 2010, identify fuel formulations optimized for use in advanced combustion engines (2010-2020) providing high efficiency and very low emissions, and validate that at least 5 percent replacement of petroleum fuels could be achieved in the following decade.

Current Status

World crude oil is becoming heavier (lower API gravity) and more sour (including greater amounts of sulfur) over time. This trend is well-established and not expected to change. Moreover, much domestic crude is heavy, such as California crude from the San Joaquin Valley. Many potential future sources of energy are heavier still, including bituminous coal and oil sands. These sources may present different refining issues than light crude and the fuels

produced from these feedstocks may differ from those for which our domestic refining industry is optimized. On the positive side, Venezuelan and domestic heavy crude use in US refineries is well-established and refining of synthetic crude derived from oil sands is growing in Canada and entering US petroleum pools. Fischer-Tropsch diesel fuels, synthesized from natural gas or coal, have been studied in numerous engine tests to determine their impact on emissions and have been used as a blending material in California diesel fuels since 1993. Use of fuels derived from biomass appears to be increasing in Europe. Exploiting some of these developments presents a significant opportunity for displacement of foreign petroleum in the US and is an important element of the NPBF activity.

More detail of the chemistries of these new fuel sources is needed and will require cooperation between DOE, national laboratories, private industry, and universities. The APBF and NPBF activities can play an important role in the pre-competitive development of these fuel sources in partnership with the energy, engine and automotive industries, and universities.

A recent workshop (2) gathered representatives of these groups and made many recommendations including:

- Research is needed to determine optimal fuel properties for advanced combustion engines
- Renewable fuels and blending components need to be analyzed on a “well-to-wheels” basis for cost effectiveness and carbon reduction
- New fuels need to be compatible with existing vehicles and fuel infrastructure

Barriers to Program Implementation

The primary goal of the APBF and NPBF activities is to identify fuel formulations with increasingly significant non-petroleum components that could replace petroleum fuels and that will enable engines and vehicles to be more energy-efficient while meeting future emissions standards. Specific barriers include:

- Inadequate data and predictive tools for fuel property effects on combustion and engine optimization
- Inadequate data and predictive tools for fuel effects on emissions and emissions control system impacts
- Long-term impact of fuel and lubricants on emission control systems
- Infrastructure and cost

The Fuels Technology Program is addressing these barriers with guidance and assistance from representatives of energy, automotive, and engine companies, industry associations, national laboratories, and universities.

Task-Based Approach to NPBF Research and Development

The program plan is being implemented with three major tasks and associated sub-tasks designed to address the barriers and specific recommendations from partner and advisor groups.

Task 1. Fuels and Lubricants to Enable High Efficiency Engine Operation while Meeting 2007–2010 Standards

- Evaluate long-term degradation and loss of effectiveness of light- and heavy-duty engines equipped with 2007–2010 technology emission control devices and using 15-ppm-sulfur diesel fuel
- Improve fundamental understanding of the effect of fuel and lubricant composition on aftertreatment systems by applying experimental and modeling approaches

- Identify fuel properties other than sulfur that are critical to improving the efficiency, performance, and emissions of light-duty diesel engines and aftertreatment systems
- Develop measurement techniques and characterize unregulated emissions from 2007–2010 engines and aftertreatment system
- Study fuels-based in-cylinder strategies to achieve high-efficiency, low-emissions operation at high power density and to improve understanding of hydrocarbon molecular structure effects on the soot generation by diesel fuel constituents

Task 2. Fuel Properties Effects on Advanced Combustion Engines

- Develop fundamental understanding of fuel effects on in-cylinder combustion and emissions formation processes in advanced combustion regimes through experimental and modeling approaches
- Develop predictive tools that relate molecular structure to ignition behavior and heat release for fuels used in advanced combustion engines
- Evaluate new fuels and fuel blends for efficiency, emissions, and operating stability with advanced combustion regimes
- Evaluate the potential of reforming small amounts of fuel to generate additives that can be used to achieve fast control in low-temperature combustion modes
- Evaluate the performance of traditional lubricant formulations in engines using advanced combustion regimes and identify any performance deficiencies

Task 3. Petroleum Displacement Fuels/ Blending Components

- Study combustion and emissions formation processes of NPBFs and blending components using experimental and modeling approaches
- Identify renewable and synthetic fuel blending components that provide enhanced efficiency, performance, and emissions characteristics
- Quantify the potential for improving engine and/or vehicle fuel economy through the use of renewable bio-lubricants
- Enhance the use of petroleum displacement fuels and NPBF infrastructure development through technical forums and by providing specialized technical support to early adopters of advanced NPBF vehicle technologies
- Review and revise appropriate codes and standards to increase the availability of petroleum displacement fuels

Summary

The Fuels Technologies program emphasizes the linkage between fuel properties and performance in advanced combustion regimes and emissions control technology, as well as petroleum displacement. Research in the program focuses on developing an understanding of fuel chemistry effects and predictive, data-based tools for fuel performance.

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FUEL EFFECTS ON SPARK ASSISTED HCCI COMBUSTION IN A GASOLINE ENGINE

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Introduction

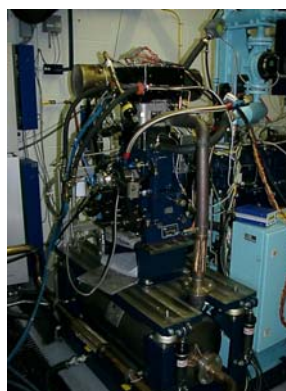
Homogeneous charge compression ignition combustion offers the potential for reduced nitrogen oxides (NOX) emissions and improved fuel economy in internal combustion engines. In this form of combustion, the fuel and air are premixed and brought to reaction conditions during the compression stroke of an engine. If conditions are just right, the fuel rapidly ignites at the right time (near top dead center) and produces work during the expansion stroke. Controlling the process generally requires a large dilution of the charge with excess air or high levels of exhaust gas recirculation to limit burn rate. This dilution also reduces peak flame temperature which results in lower NOX generation. Some form of additional energy input is also used to control reaction kinetics, often taking the form of intake temperature control. Heat release is faster than conventional IC engine combustion and can result in improved fuel efficiency. Since the fuel ignition process is kinetically driven, fuel properties also play a large role in the process. In various forms, this technology can be applied to gasoline, diesel, or natural gas fueled engines. The main barriers to the implementation of this combustion technology are stability and control and operation at low and high engine speeds and loads. There is a large amount of research being conducted in these areas.

The work described in this presentation was conducted in a single cylinder, port fuel injected, spark ignited research engine equipped with hydraulically actuated variable valve timing. HCCI combustion was initiated by early closing of the exhaust valve to retain exhaust in the cylinder, adding both increased temperature and pressure to the subsequent compression and combustion processes. Four gasoline range fuels were investigated which varied primarily in their motor octane number (MON). Trends were found that higher MON resulted in slower combustion, lower peak pressures, improved fuel efficiency, and lower NOX emissions. These trends may also show some fuel chemistry or property effects which could not be sorted out with the number of fuels tested. Other work was done relative to spark assist of HCCI combustion to improve operating range, stability, and control.

Experimental Work

A photo of the engine and main attributes are shown in Figure 1. Data was taken at a variety of speed, load, and timing conditions, but only data from 1600 rpm and 3.0 bar indicated mean effective pressure (IMEP) will be presented here. This condition represents a part load condition typical of US passenger car engine operation. All tests were run at stoichiometric fuel / air ratio ($\lambda = 1$). This engine is located at AVL Powertrain Engineering, Inc. in Plymouth, MI and was operated under sub-contract to ORNL.

The test rig was equipped with a complete emissions bench, combustion pressure analysis, and the normal complement of engine instrumentation. Intake and exhaust valve timing and lift, spark timing, and fuel injection quantity were controlled with test cell automation and could be varied with the engine in operation.



- Capable of HCCI, mixed mode, and conventional operation
- 500 cc, 11.34 C/R
- 2 valves, naturally aspirated
- Gasoline port fuel injection
- Spark ignition
- Fully variable valve actuation
- HCCI initiated by early exhaust valve closing
 - Retains heat in cylinder
 - Internal EGR
 - Typically operates at > 50% EGR

Figure 1. Single cylinder research engine with list of main attributes.

Analysis of this engine is somewhat complex because exhaust is retained in the cylinder rather than externally recirculated, so that it is difficult to measure. There are also confounding effects between total mass, heat, pressure, and residual gas composition. The engine was operated in conventional combustion mode as well in order to document performance improvements from HCCI operation. Figure 2 presents a comparison of engine operation in conventional and HCCI modes, and this figure also helps explain the operation of the engine in HCCI mode. In addition to varying the exhaust valve closing to trigger HCCI, intake valve opening is also varied in a symmetric way.

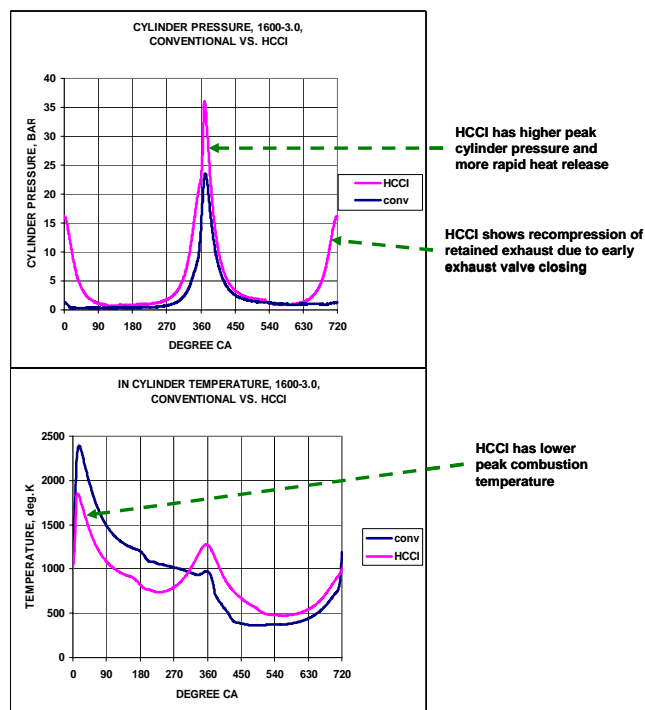


Figure 2. Comparison of engine operation and performance in conventional and HCCI modes.

Although not a subject of this presentation, over the speed and load range tested, the engine averaged 12% more fuel efficient and produced 95% less NOX in HCCI mode compared to conventional operation. Spark assist was found to extend the range of operation

and to assist in the transition from conventional to HCCI combustion. All data presented here is with spark assist active.

Four fuels were evaluated for their effect on HCCI engine operation. These fuels included an indolene base fuel and three fuels blended from pure hydrocarbon compounds. Fuels varied primarily in their MON values, but there were also differences in fuel chemistry and other properties. Fuel properties for the four fuels are shown in Table 1. The blended fuels were obtained from a major oil company who is assisting with this research.

Table 1. Properties of Fuels Tested

FUEL	RON	MON	DENSITY, 60F	RVP, PSI	GROSS HEATING VALUE, BTU/LB	IBP, C	FBP, C	FUEL BLEND
indolene	96.5	88	0.745	8.3	19550	31	198	full boiling range
fuel 1	97.4	80.9	0.822	3.8	18867	62	110	4 pure HC
fuel 2	99.5	86.8	0.76	3.2	19647	72	117	5 pure HC, 50% #1 and #3
fuel 3	96.3	94.5	0.695	1.9	20487	98	104	2 pure HC - PRF

Results and Discussion

The combustion characteristics of the engine in conventional and HCCI combustion is best understood by running a series of test points with varying exhaust timing to transition the engine from conventional to HCCI mode. As more exhaust is retained in the cylinder (earlier exhaust valve closing), NOX output drops due to the resulting lower peak cylinder temperature. Compression pressures and temperatures increase until the engine transitions to HCCI combustion. At this point, duration of heat release (10 to 90% burn) drops from 20 to 30 deg. CA to less than 10 deg. CA, ISFC improves, and peak cylinder pressure and rate of pressure rise increase. In HCCI mode, the spark has only a small effect and the engine will continue to run if the spark is turned off. Combustion is initiated kinetically and 1% heat release takes place at 22.1 ± 0.2 bar cylinder pressure and 995 ± 20 deg.K cylinder temperature for indolene at 1600 rpm, 3.0 bar IMEP. This can be considered to represent the combustion conditions required for this fuel. Some of this verbal engine operation description can be visualized by examining Figure 2.

The four fuels were compared by running a group of test points in HCCI mode and comparing results obtained. The data presented represents an average of four sets of 160 engine cycles. The fuels were compared for both combustion characteristics and engine performance. Data is shown in Figure 3. General trends show that with higher MON, NOX and ISFC improve and combustion pressures and heat release rates are lower. Interestingly, all fuels show the same cylinder pressure at 1% heat release indicating similar ignition temperature characteristics. The trends with MON are not monolithic, and the two center fuels are reversed in their behaviors. This may be due to some other fuel property or fuel chemistry effects since indolene is a fully range fuel, while fuel 2 is blended from only 5 pure hydrocarbons. More fuels would be necessary to test this hypothesis.

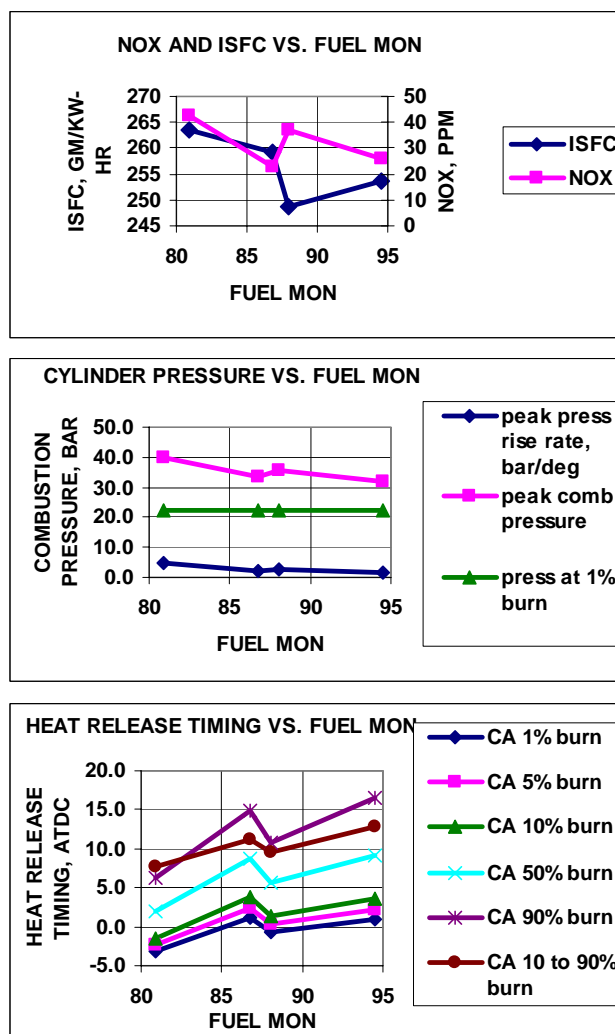


Figure 3. Combustion and Performance Results for Four Fuels.

Conclusions

An evaluation of four gasoline range fuels in a spark assisted HCCI engine showed combustion and performance characteristics trending with fuel MON. General trends show that with higher MON, NOX and ISFC improve and combustion pressures and heat release rates are lower. All fuels started heat release under similar cylinder conditions. The engine was also run in conventional mode and HCCI was found to have improved fuel efficiency and reduced NOX.

Acknowledgement. This work was supported by U.S. Department of Energy, Energy Efficiency and Renewable Energy Division, Steve Goguen and Kevin Stork program managers. The engine work and combustion analysis were performed by AVL Powertrain Engineering, Inc. in Plymouth, MI under subcontract to Oak Ridge National Laboratory. We would also like to acknowledge assistance obtained from a major U.S oil company in fuel blending, advice, and assistance with data interpretation.

THE HIGHLY EFFICIENT INTEGRATED PLASMA FUEL CELL (IPFC) ENERGY CYCLE FOR CONVERSION OF FOSSIL AND BIOMASS FUELS TO ELECTRIC POWER GENERATION AND HYDROGEN AND LIQUID TRANSPORTATION FUEL PRODUCTION WITH REDUCED OR ZERO CO₂ EMISSION

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Introduction

In an earlier paper [1] the IPFC is principally applied to electrical power production. In this paper the IPFC is applied as a co-producer of electricity and hydrogen and/or transportation fuel (i.e., gasoline and diesel). The basic concept is the integration of the Hydrogen Plasma Black Reactor (HPBR) [2-3] with the Direct Carbon Fuel Cell (DCFC) [4-6]

The HPBR decomposes any dry carbonaceous fuel to elemental carbon and gaseous H₂ and CO. Since no oxygen or steam is used in this gasification reactor, CO gas is only formed when oxygen is present in the feedstock, as in coal and biomass fuel. Since the temperature in the thermal hydrogen arc is very high (~1500°C) the conversion to elemental carbon and gaseous products is near 100%. Because the thermodynamic energy of decomposition of the feedstock fuel is small compared to the heating value of the feedstock, the thermal efficiency is found to be over 90%.[2-3] This means that the electrical energy requirement for the HPBR is very small. Based on the thermodynamic energy (enthalpy) of decomposition of natural gas and petroleum, the electrical energy efficiency (process energy efficiency) was determined to be 60% for an industrial unit.[3] Although, the specific energy requirement for decomposition of solid fuel (coal and biomass) is yet to be determined, this process efficiency was applied to the thermodynamics of decomposition of these feedstocks. It should also be noted that the thermodynamic energy (enthalpy) of decomposition is less for petroleum than for natural gas and coal is less than for petroleum. Other plasma reactors have been operated for steam gasification of solid fuels, however, these required higher power inputs because the steam gasification reactions are highly endothermic, requiring higher electrical energy inputs.[10] Due to the much lower endothermicity of the thermal decomposition reaction and operation in a dry hydrogen atmosphere the HPBR requires much less energy than the plasma steam gasifier.

The elemental particulate carbon is separated from the gas stream cyclonically or by asbestos bag filters or by absorption directly into a molten carbonate salt stream. The latter is preferred since the Direct Carbon Fuel Cell (DCFC) operates with a molten carbonate electrolyte. The ash should form molten agglomerates, which can be separated from the carbon particulates cyclonically or gravimetrically in a fluidized bed. The carbon/molten salt slurry is sent to the anode compartment of the DCFC and air is fed to the cathode. The mixed molten carbonate salt (Na, K salts) acts as the electrolyte operating at 700-800°C. The carbonate ion carries the electrons from the cathode to the anode compartment through a membrane, which then reacts with the carbon at the anode releasing undiluted CO₂ gas thus completing the electrical fuel cell circuit. Voltage efficiencies of 80 to 90% have been obtained with amorphous carbon at reasonable current densities (0.2-0.8 Kw/M²).[4-6] The overall reaction in the DCFC is the oxidation of carbon to CO₂, the theoretical thermodynamic efficiency of which is 100% since the entropy change for the reaction is zero.

The combination of HPBR with DCFC is unique in that no

outside source of electricity is necessary to drive the process. The DCFC supplies the HPBR with electrical power and the HPBR supplies the carbon for operation of the DCFC. The high efficiency of the DCFC and the relatively low power requirements for the HPBR produces a highly efficient integrated system for electrical power generation. The gases from the HPBR after cleaning can be used to produce either H₂ or syngas depending on the type of feedstock used.

The flowsheet for hydrogen production is completed by adding a water gas shift (WGS) reactor to convert the CO to hydrogen and CO₂ with the addition of steam (water). The CO₂ is separated by membrane or absorption/stripping and a clean pure H₂ stream is produced for sale.

Alternatively the syngas can be water gas shifted either forward or reverse (depending on the feedstock) to produce a stream in which the ratio of H₂/CO is 2.0 for feed to a Fischer-Tropsch catalytic converter to produce either gasoline (C₈-C₁₁ average C₈H₁₈) or diesel (C₁₁-C₂₁ average C₁₆H₃₄) [7,8,9] transportation fuel. Figure 1 shows the IPFC-FT flowsheet.

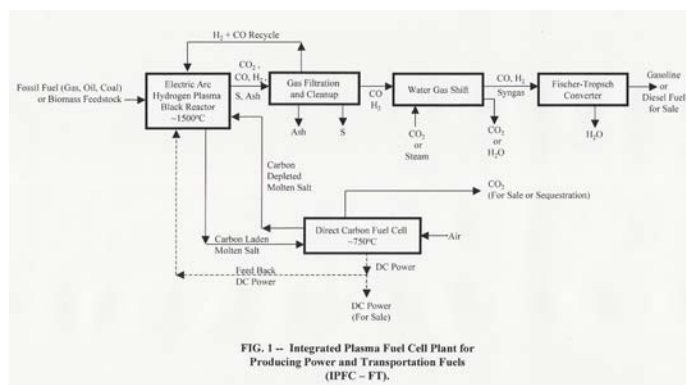


FIG. 1 – Integrated Plasma Fuel Cell Plant for Producing Power and Transportation Fuels (IPFC – FT).

For reverse shift the CO₂ can be obtained from the DCFC. Note that using the higher heating value, the water gas shift reactions are essentially energy neutral ($\Delta H \approx 0$). The exothermic reactions in the Fischer-Tropsch catalytic reactor are represented by the following typical reaction with the unit CH₂ representing the unit hydrocarbon fuel molecule: $2H_2 + CO = CH_2 + H_2O$. Typically, the enthalpy of reaction is $\Delta H = -49.5$ Kcal/gmol of unit CH₂, exothermic

Energy Efficiency of IPFC

Using thermodynamic data for each of the feedstocks, the thermal efficiency of the IPFC is defined as follows: The Output Electrical Energy + Higher Heating Value of the Transportation Fuel (H₂ or CH₂) divided by the HHV of the feedstock for 5 fuel feedstocks. Integrated together with the assumed reactor efficiencies, the calculated thermal efficiencies for electricity and hydrogen production range around the 90% value.

Table 1 gives the mass and energy balances and the thermal efficiencies for electricity and transportation fuel production using the IPFC-FT cycle. The efficiencies range from 70% to 83% for the 5 feedstocks studied in this paper. The liquid hydrocarbon transportation fuel can be used in current internal combustion engine vehicles and in the recent gas-electric hybrids as well as in other automotive vehicles that will be developed in the future to increase miles/gal (mpg) efficiency. The benefit of liquid fuels is that the current infrastructure for distribution, storage and engines are in place, which is not the case for hydrogen as an automotive fuel in fuel cell vehicles.

Table 1
Integrated Plasma Fuel Cell (IPFC) Cycle
Electrical Power and Transportation Fuel Production
Mass and Energy Balances and Thermal Efficiency
Basis – 1 gmol of Feedstock Fuel

Fuel Feedstock	Natural Gas	Petroleum	N. Dakota Lignite Coal	Kentucky Bit. Coal	Biomass (wood)
Molar Composition (MAF) (MW)	CH ₄ 16.00	CH _{1.7} 13.70	CH _{0.77} O _{0.24} 16.61	CH _{0.81} O _{0.08} 14.09	CH _{1.38} O _{0.81} 22.82
Plasma Decomp. Products Mole/Mole Fuel					
C	1.0	1.0	0.76	0.92	0.41
CO	0	0	0.24	0.08	0.59
H ₂	2.0	0.85	0.385	0.41	0.69
Ash, S, N (wt%)	-	-1.0	9.8	12.6	1.1
Enthalpy of Decomp. Kcal/gmol feedstock	18.0	3.0	3.6	4.8	12.7
Water gas shift, (WGS) gmol CO ₂ and H ₂ per mol feed to obtain H ₂ /CO = 2.0	0.667	0.283	0.032	0.083	0.163
Transportation Fuel Production Gasoline or Diesel gmol CH ₂ /mol feed	0.667	0.283	0.208	0.163	0.427

Electric Power and Transportation Fuel Production Enthalpy Energy Values in Kcal/gmol Fuel					
Unit	Eff%				
DCFC	90	84.6	84.6	64.3	77.8
WGS	100	-	-	-	-
HPBR consumed	60	-30.0	-5.0	-6.0	-8.0
Net Electricity Prod.	54.6	79.6	58.3	69.8	13.5
F-T Gas, Diesel Fuel*	103.5	43.7	32.1	25.2	66.0
Total Energy Output	158.1	123.3	90.4	95.0	79.5
HHV of Fuel Feedstock	212.0	149.0	110.3	119.0	112.8
Thermal Efficiency %	74.5	82.8	82.0	79.8	70.4

*HHV of gasoline and diesel fuel = 154.5 Kcal/gmol

The CO₂ emissions from IPFC are compared to that of an equivalent IGCC plant providing the same quantity and ratio of product electricity and hydrogen output. Estimates of the efficiency of the IGCC vary from 54 to 72% while the IPFC efficiencies range from 87 to 92%. As a result, the CO₂ emission reduction for IPFC is from 20 to 40% less per unit energy in the products than the IGCC. Furthermore, CO₂ emitted from the IPFC is undiluted ready for sequestration. Whereas for IGCC, the CO₂ is diluted with nitrogen and steam.

The CO₂ emission reduction for IPFC at 82% efficiency compared to IGCC at 60% efficiency when electricity and transportation fuel (gasoline or diesel) are produced in the same relative amounts, when using a lignite coal is 26% lower than for IGCC. Compared to a coal burning steam plant generating power at 38% efficiency, the IPFC plant shows a 76.4% reduction in emission of CO₂ per unit of electricity. There is a 36.4% reduction in CO₂ for IPFC producing gasoline compared to a gasification synfuel plant producing gasoline alone.

Preliminary economic estimates (11) indicate that IPFC plants can produce electricity and hydrogen or transportation fuels at a significantly lower cost than conventional steam and combined cycle plants (NGCC and IGCC). Furthermore, production of two co-products permits adjusting the sale price of electricity upwards to meet current market price, which allows adjusting the price downward of the co-product IPFC synthetic transportation fuel to allow direct competition with current oil refinery production prices.

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FINDING FUELS FROM THE LAND – THE POTENTIAL FOR A LARGE SCALE CONTRIBUTION OF BIOMASS

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Introduction

The estimation of future biomass supplies for large scale fuels, chemicals and electricity production is confounded by the many ways in which biomass is generated and used. Today the biomass for energy stream is composed of residues from primarily industrial and societal activities. In the absence of major technological breakthroughs, future large scale use will require that land be allocated to feedstock production, and possibly will call for significant changes in the food, feed and fiber production systems through the introduction of multi-functional cropping systems that simultaneously meet demands for traditional uses as well as energy. Thus, the production of biomass feedstocks, and bioenergy use is today very dependent on the functioning of some other components of the economy -- the three major areas being forestry, agriculture, and the urban environment. As time goes on this dependency will become more strongly integrated with these sectors.

Source of Bioenergy

To simplify the discussion of biomass, it is necessary to provide some definitions and characterization of where in the economy biomass is generated or utilized as bioenergy. One methodology is to identify the stage of processing/utilization since the creation of the biomass by photosynthesis. Energy crops are a primary supply and involve the production and growth of biomass specifically for biomass to energy and fuels applications. Primary production is widespread in developing countries for fuelwood, as well as examples of Eucalypt forestry for charcoal production in iron production in Brazil [1]. Also in Brazil a significant fraction of the sugar cane crop is dedicated to ethanol production [2], while 9% of the corn harvest in the United States is used in the production of ethanol from starch [3]. Research and development in Europe and the United States is developing the use of woody or straw materials (lignocellulosics) as high yielding non-food energy crops. Primary residues are produced as a by-product of a primary harvest for another material or food use of grown biomass. A representative of this is the use of tops and limbs as well as salvage wood from forestry operations cutting saw-logs or pulpwood. This material along with forest thinning is a developing biomass supply system in Finland, for example [4].

Secondary and Tertiary Residues

The majority of biomass used today in the energy system is generated as secondary and tertiary residues. Secondary residues arise during the primary processing of biomass into other material and food products. Sugarcane bagasse is widely used to fuel combined heat and power plants (CHP) providing the heat and electricity needs of sugar processing as well as export of electricity to the grid. In the forest industries black liquor from kraft pulping is a major fuel for CHP and the recovery of process chemicals. The meat, dairy and egg production in concentrated animal feed operations (CAFO) is a rapidly growing area in which bioenergy production is part of the solution to environmental issues created by this landless food production system.

Tertiary residues, urban or post consumer wastes, are a major component of today's bioenergy system. In fact the official statistics of the IEA, for example, describes biomass as combustible renewables and waste, and in many countries the tertiary sector is captured under the title of municipal solid waste or MSW. The tertiary sector generates energy in combustion facilities as well as from the generation of methane as land fill gas (LFG) from properly managed burial of mixed wastes from cities. Methane is also produced in sewage treatment facilities. Individual rates of residue generation are currently about 22 MJ person⁻¹ d⁻¹ in the United States. This, combined with the high population densities of metropolitan areas, results in very high bioenergy potentials in this sector [5]. Currently, MSW and landfill gas contribute about 0.5 EJ of primary energy in the United States [6].

U.S. Projection

There is a consensus biomass resource potential estimate for 2020 in the U.S. that captures most of the sources described above, other than the CAFO potential [6]. This is described in the form of a supply curve and indicates that there are about 7 - 8 EJ of primary energy at less than 4.0 \$ GJ⁻¹. This represents about 450 Mt of dry lignocellulosic biomass potential, which can be compared with today's utilization of about 190 Mt. The ultimate technical potential for biomass in the United States is not yet established, however, work is underway on what is called the Gigatonne scenario, which would investigate the effect of seeking double the 2020 projection for say the 2040 - 2050 period.

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Technology Advances in Biobased Fuels

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Introduction

In 2001 consumption of biodiesel (diesel from soybeans and other oil feedstocks) reached 20 million gallons and in 2003, ethanol production from starch topped 2.8 billion gallons. Both biobased fuels have had a long road to the limited percentage they have now in the fuel pool. Ethanol is roughly 2% of the gasoline pool and biodiesel is less than 0.5% of the diesel pool, and both are primarily used as additives. But new governmental and corporate policies are indicating that this is not just the beginning of biobased fuels but also biobased chemicals and materials. The demand for green but sustainable and profitable biobased products must lead to new feedstocks that are cheaper and more abundant, and the technologies to utilize them efficiently and economically. This paper discusses some of the recent advances in biochemical technology to convert biomass, specifically lignocellulosic biomass (i.e. non-starch biomass), to ethanol. This is a portion of the work being done under the Office of the Biomass Program (OBP) in the US Department of Energy and also in the private sector. Not discussed here, but equally important, are advances in syngas catalyst development and modular, distributed gasification systems that are components of OBP's thermochemical program.

The Advantages of Biobased Fuels

Fuels from lignocellulosic biomass reduce oil consumption and greenhouse gas emissions. A comprehensive study by NREL and a consortia of feed and soil experts found that "for each kilometer fueled by the ethanol portion of E85, the vehicle uses 95% less petroleum compared to a kilometer driven in the same vehicle as gasoline."¹ E85 is a blend of 85% ethanol and 15% gasoline. It is currently available in limited supply in the US for use in a FFV, or flexible-fuel vehicle, like the Ford Taurus. The energy balance (energy used to produce the fuel vs. energy in the fuel) from a life cycle assessment is positive for both starch² and lignocellulosic ethanol. Life cycle assessment results depend heavily on the data and boundaries used, and conflicting numbers have and will continue to be reported, but the value of these analyses is an increased understanding that practices in growing, collecting and processing the biomass can be optimized to reduce the fossil energy use and maintain the soil health.

Overcoming the Challenges of Biomass Conversion

Variability of biomass composition, recalcitrance to depolymerization and metabolism, and solids handling are a few of the key challenges to making biomass conversion technically and economically feasible.

Biomass Composition. Lignocellulosic biomass is a complex and non-standard feedstock. It contains a mix of long chain compounds, the fractions of which vary as a result of genetics, growing conditions, and collection methods. **Table 1** summarizes the primary constituents in biomass, such as agricultural residues (corn stover or straw), forest and mill residues, energy crops such as switchgrass and urban waste. Understanding and predicting the effect this variability has on processing needs is key to efficiently converting biomass via biochemical or thermochemical routes. Near infrared analysis (NIR) methods are being developed to infer the biomass composition quickly and cheaply. This will enable a

"carbohydrate" or "carbon" biomass economy in which feedstocks are valued on these fractions, and processes can be optimized with feed-forward control.

Table 1. Major Components of Lignocellulosic Biomass

Component	Amount	Description
Lignin	15-25%	-Complex aromatic structure -Resists biochemical conversion -Requires high temperatures to convert
Hemicellulose	23-32%	-Polymer of 5 and 6 carbon sugars -Easily depolymerized -5 carbon sugars difficult to metabolize
Cellulose	38-50%	-Polymer of glucose -Semi-crystalline structure -Susceptible to enzymatic attack -Glucose easy to metabolize

In **Figure 1**, the measurement of several corn stover (the stalks, leaves and cobs) components via both NIR and wet chemical methods shows good correlation between the two.

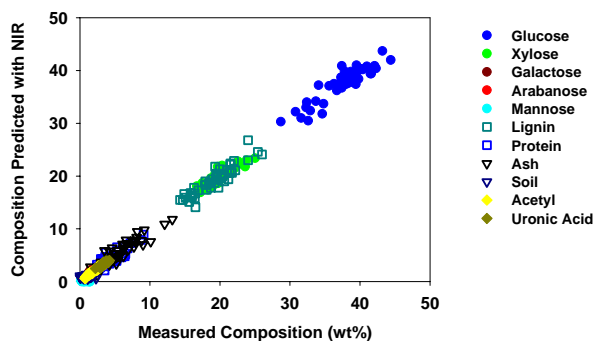


Figure 1. Correlation of NIR with wet chemistry methods for stover.

Recalcitrance to depolymerization. The highly linked structures of biomass make it resistant to depolymerization. Advances in both the thermochemical and biochemical methods of depolymerizing biomass include continued development of a host of various pretreatment methods that could suit certain feedstocks better than acid methods or create a new and different process intermediate. Through multi-year partnerships with Genencor and Novozymes Biotech, leading enzyme companies, the cost of cellulase, the catalyst for depolymerizing cellulose, has been reduced over 10 fold. The significance of the cost reduction in terms of its contribution to ethanol production cost is seen in **Figure 2**.

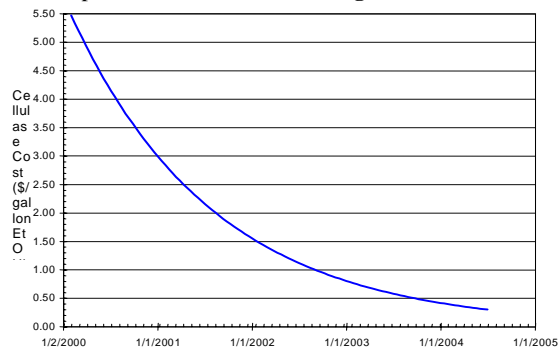


Figure 2. Cellulase enzyme cost reductions.

Solids handling. Maintaining a high solids loading throughout any process decreases the size of equipment and can reduce the capital cost of the plant. High solids pretreatments have been performed in the NREL pilot plant up to 35% solids, which reduces the cost of downstream equipment by as much as \$0.18 per gallon ethanol from a 20% solids loading.

The Cost of Producing Ethanol from Biomass

Process configurations, mass and energy balances, and cost estimates provide quantified snapshots of the state of different biomass conversion technologies. NREL routinely develops process information like that shown in **Figure 3** to illustrate what portions of the process contribute the most to the production cost – this particular example is for an ethanol process using dilute acid.

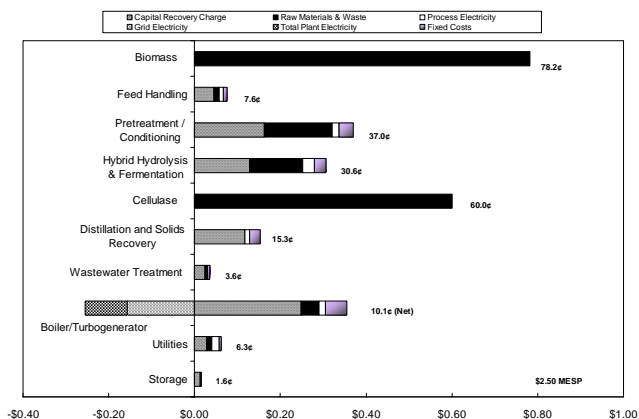


Figure 3. Estimate of current state of dilute acid technology

The other necessary picture to have is the target – where the R&D program is headed and what constitutes success. **Figure 4** shows the costs by process area of ethanol production from a dilute acid/enzymatic hydrolysis process for a production target of less than \$1.10 per gallon ethanol, sufficient to compete in the corn ethanol market. Although there are many ways to get to a cost target, having at least one baseline pathway shows that the process is technically and economically feasible with appropriate R&D in the key areas. This target case was published in 2002 by NREL.³

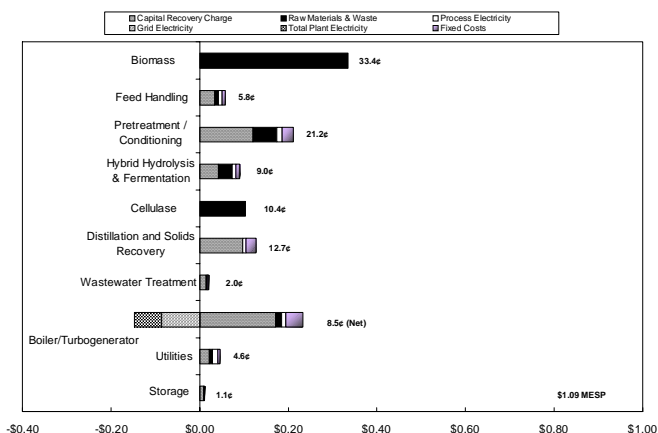


Figure 4. Target for entry into ethanol market.

Biorefineries

The biorefinery concept is considered by many to be the best way to boost the economic viability of biobased fuels. Its premise is that by adding high value chemicals from biomass (either starch or lignocellulose) to the product slate from an ethanol plant, one can

buy-down the cost of producing the ethanol. Added to this is the benefit of producing biobased chemicals, which is becoming increasingly popular in both governmental and industry arenas for a variety of reasons including reducing the environmental footprint of chemical production. **Figure 5** shows one possible configuration for a biorefinery utilizing both biochemical and thermochemical conversion. Several companies including Dupont, Cargill, Cargill Dow and Dow have projects underway, some co-funded by DOE's OBP to develop these emerging biorefineries. Other companies that currently produce corn ethanol like Aventine Renewable Energy, Broin Companies and Abengoa Bioenergy, are developing value-added products from the solids stream resulting from corn ethanol production. These plants represent the current generation of biomass biorefineries that could also include the forest products industry.

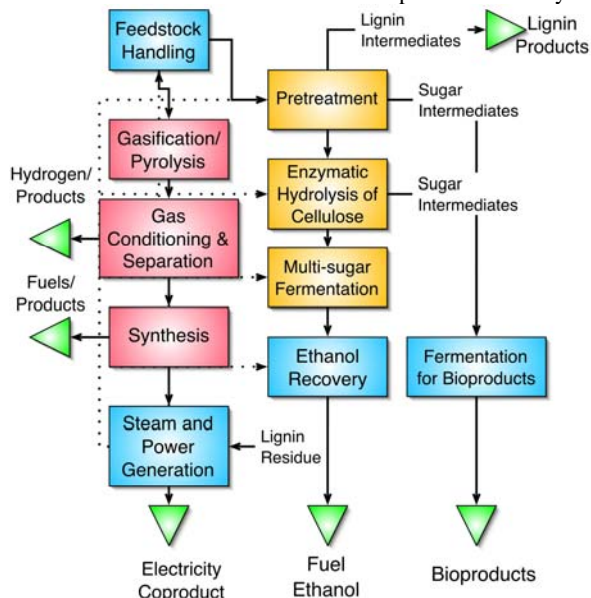


Figure 5. One biorefinery concept for lignocellulosic feedstocks

Conclusions

Affordable cellulases, varied pretreatment options, a fundamental understanding of biomass feedstocks, and capital cost reductions are all areas where significant advances are being made to make biomass conversion technology more technically and economically viable. Biorefinery concepts may enable integration into existing dry mills and eventually lead to stand alone facilities that produce fuels and other products from biomass. Thermochemical processes like gasification and pyrolysis provide diversity in processing and as such, enable a larger set of industries to utilize biomass.

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RUNNING ON EMPTY REVISITED: LESSONS OF THE PAST FOR FUELS OF THE FUTURE

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Introduction

Why hasn't more been accomplished in the last quarter of a century to solve America's energy problems? How long does it take to deploy fuel and energy alternatives? And, why does America, the most technologically advanced nation in the world, continue to have serious problems with fuel and energy supplies? To address these questions, the authors draw upon the extensive research that was the basis of the public radio documentary *Running on Empty: America's Energy Crisis*. The documentary traced history through the twentieth century to the roots of America's current energy crisis; surveyed current resources, consumption patterns and energy infrastructure; examined energy policy; and then looked ahead to see how conservation, new technology and untapped resources could help solve the U.S. energy crisis. In researching and producing the program, we found many lessons of the past that may aid in dealing with today's energy issues.

If development of technology were the only factor required to bring new fuels to the marketplace, America would have no shortage of fuel and energy supplies today. Obviously, this is not the case. Technology resulting from research and development (R&D) is just the first step of many processes involved in the deployment of new fuels and energy supplies. The issues involved in bringing fuel and energy technology to the marketplace are complex and integrated with our culture, economy, government, environment, and political system. In this short paper, we review a few significant lessons of the past to see how these may guide today's approaches for developing policy and deploying new technology for transportation fuels.

Running on Empty – the Documentary's Context and Content

We produced the public radio documentary *Running on Empty: America's Energy Crisis*, underwritten by the American Chemical Society's Fuel Chemistry Division, in response to a re-emerging energy crisis at the turn of the twenty-first century. After nearly two decades of a seemingly plentiful energy supply, Americans were again concerned about energy issues. Californians, especially, faced a major energy crisis. Attendees of the 2001 Spring National ACS Meeting in San Diego, California may recall the high level of public anxiety at the time. Californians were worried sick about the rolling electricity blackouts and the cost of natural gas and gasoline. Public apathy regarding energy issues had suddenly ended, at least in California.

While at the San Diego ACS meeting, there were daily news reports of business and school closings, and car crashes caused by traffic signal lights failing due to rolling electricity blackouts. ACS meeting attendees found flashlights on conference room tables with notes reminding them that blackouts could prevent speakers' presentations. Californians were deeply concerned about losing their jobs and the impact of a looming recession. They were experiencing in very real and personal economic terms just what fuel and energy shortages meant. Yet, news broadcasts reported only the effects of the crisis. They contained little information about the causes that would help the public to understand the developing energy crisis.

We asked ourselves: Why does America, the most technologically advanced nation in the world, continue to have serious energy problems? Why haven't Americans insisted on a long-term commitment to deal with the nation's energy woes?

We felt that America's complacency toward energy was, in part, due to a lack of public understanding of energy issues and the technological developments that could provide options to help solve current energy problems. We decided to try to fill a portion of that information void with a documentary on energy.

Production of *Running on Empty* required months of research, thirty hour-long recorded interviews with experts ranging from scientists to politicians resulting in over four hundred pages of transcripts. After completing script writing, audio production, and editing, and compact disc mastering, the program made its debut in May of 2001 on public radio station KUNM FM 89.9 in Albuquerque, New Mexico.

During 2001 to 2003, *Running on Empty* aired on over 100 public radio stations nationwide representing a service area population of 100 million. The documentary received national awards for excellence in broadcast journalism. And, the nation's largest non-religious organization, the American Automobile Association, endorsed *Running on Empty* as "Energy 101 for motorists." The following is a synopsis of the content of the documentary.

- The first segment - *Why Are We Running on Empty?* - weaves audio from archived newscasts with interviews and the thoughts of the person-on-the-street, to trace history through the twentieth century to the roots of America's current energy crisis.
- Through extensive interviews of energy experts, the second segment - *Where Are We Now?* - paints a picture of the current American energy landscape--our resources, consumption patterns, infrastructure, and the factors that shape costs.
- *Who's at the Wheel?* - the third segment - examines energy policy through the eyes of politicians, political scientists, economists and stakeholders, to see how public and national interests, environmental concerns, and market forces are balanced.
- In the last segment - *Driving the Future* - scientists, engineers, and strategists give their views on how conservation, new technology and untapped resources can solve our energy crisis.

We found that the research forming the basis for the content of the documentary was equal to the public outreach value. Contained in the documentary and the four hundred pages of transcripts were many lessons of the past regarding the social, political, technological, economic and environmental responses to America's voracious energy appetite.

Running on Empty Revisited—Lessons of the Past

"Our decision about energy will test the character of the American people and the ability of the President and the Congress to govern this nation. This difficult effort will be the 'moral equivalent of war'. . ." Some may remember those words spoken by President Jimmy Carter as he declared war on the nation's energy crisis in 1977. However, after a quarter of a century, we are still facing our energy woes, as spotlighted by President Bush in his first State of the Union address, January, 2001: *"We have a serious energy problem that demands a national energy policy."*

Perhaps the most serious energy problem America has faced over the past quarter of a century is dependence on foreign petroleum for our transportation fuels. At the time of the fuel crisis of 1973, triggered by the OPEC oil embargo, U.S. imports [1] amounted to 37% of our total supply (17 million barrel/day). Today America

imports 56% of its supply (20 million barrel/day) [2]. The vulnerability to fuel supply shortages and price spikes is obvious.

As Philosopher George Santayana wrote: "Those who cannot remember the past are condemned to repeat it." If we'd remembered the energy lessons of the past, perhaps we would be much farther ahead in solving our transportation fuel problems. With continued rumblings of major energy problems, it is appropriate to revisit *Running on Empty*, the documentary, to examine the past and some of its lessons.

1. R&D provides options, not solutions. During the decades following the energy crisis of the 1970s, thousands of scientists and engineers contributed to U.S. Department of Energy and private industrial programs to augment U.S. energy supplies. They played the crucial role of providing a portfolio of new technology options through their R&D efforts. However, until energy technology is deployed and begins to make a significant contribution to energy supply problems, it remains an option, not a solution.

After proven to be technically feasible by scientists and engineers, new technology faces many challenges. To be successful, new technology, must pass tests of cost effectiveness, environmental and social acceptability, and compatibility with current energy infrastructure.

The following are two examples of new fuel technology options that scientists and engineers have added to the U.S. fuel portfolio since the 1970s. These are demonstrated to be either economically feasible or nearly so. A brief status of each is given with respect to deployment.

Liquid fuels from coal. Over the past three decades, \$1.7 billion of government R&D has been invested in developing processes to convert coal, America's most abundant fossil energy resource, to liquid transportation fuels. The latest process concepts, called co-production, combine coal gasification with slurry phase Fischer Tropsch synthesis and electric power generation to achieve high efficiencies. Cost analyses of conceptual processes, based on the operation of commercially available components, show that liquid fuels (diesel and naphtha) from coal can be produced for about \$35 dollars a barrel [3]. Compare this to the current price of petroleum of \$41/barrel as of May, 2004. Additionally co-production processes are much cleaner and much more efficient than previously developed coal liquefaction technology.

Two DOE demonstration projects are planned. No commercial plants have been built, largely because of the fluctuating price of oil and the large capital investment required. An investment of about one billion dollars is required to construct a plant that produces 30,000 barrel/day of diesel and naphtha, AND generates 700 MW of electricity. Coal co-production, as with the use of all fossil fuels, including petroleum and natural gas, faces environmental compatibility challenges, including the issues related to reducing greenhouse gas emission of CO₂.

Biofuels. Two biofuels ethanol (grain alcohol) for spark ignited engines and biodiesel for compression ignited engines have entered the fuels market.

Ethanol is extensively used as a gasoline oxygenate additive (a mixture of 10% ethanol in gasoline, called E10) to reduce tailpipe emissions. By the end of 2004 U.S. fuel ethanol production capacity will be 3.4 billion gallons—most of this used for E10. This may be compared to U.S. annual gasoline consumption of 132 billion gallons [1]. In 1996 a new fuel called E85 (85% ethanol, 15% unleaded regular gasoline) was introduced as were cars called flexible fuel vehicles (FFVs) that can run on E85, gasoline or any mixture of the two. For 2004 the "big three" and other automakers are marketing twelve models. There are 3.5 million FFVs on the road today. Even though E85 is the fastest growing fuel market in the U.S., annual consumption amounts to only 22 million gallons. With tax

incentives, E85 is cost competitive with regular gasoline. Currently ethanol is produced primarily from crops that yield starches or sugars. R&D efforts are now focusing on producing ethanol from biomass sources such as wood and animal wastes.

Biodiesel consists of fatty acid alkyl esters produced from soybeans and other vegetable oil feedstocks. Annual production capacity is about 70 million gallons, compared to U.S. annual total petroleum distillate consumption of 38 billion gallons [1]. Biodiesel operates in compression-ignition engines, just like petroleum diesel. Blends of up to 20% biodiesel (mixed with petroleum diesel fuels) can be used in nearly all diesel engines and are compatible with most storage and distribution equipment. Biodiesel offers advantages of improving low sulfur petroleum fuel lubricity and lowering tailpipe emissions.

It is clear from these examples that the scientists and engineers have done their jobs. Their R&D efforts since the energy crises of the 1970s have provided a portfolio of new alternatives to petroleum-based fuels. It is now time for the political, governmental, commercial and public sectors to bring these fuel technologies to the marketplace.

2. Change occurs incrementally. One of the most important lessons of the past three decades was pointed out in our interview of Professor Don E. Kash, author of the definitive book, "U.S. Energy Policy – Crisis and Complacency" [4]. Professor Kash stated [5]: "It seems to me that if there's any message of the last 30 years, in connection with energy, is that the energy system is big, complex, and adaptation has to occur incrementally."

Energy system inertia. Why does change in our energy system occur incrementally? To answer this we apply the term "inertia"—the tendency of a system to remain at rest, if at rest; or if moving to keep moving in the same direction unless affected by an outside force. The enormous size of America's energy infrastructure, mostly a fossil-fueled energy system, represents a huge amount of inertia.

For example, the world's capital investment in energy represents a replacement cost of ten trillion dollars, with an average lifetime of facilities of 30 to 40 years. From a business perspective, the energy industry is represented by large powerful commercial interests vested mainly in oil, gas, electricity, coal, and nuclear energy. Three of the top seven Fortune Five Hundred companies are fuel and petrochemical producers representing annual revenues of \$424 billion. From a political perspective, Representatives and Senators from energy producing states dominate key congressional committees that develop energy legislation and policy. For example, 15 of the 23 members of the Senate Energy and Natural Resources Committee represent fossil energy producing states. And there are myriad energy policies on the books that literally take acts of Congress to change.

Historical timescales for deployment of new fuels. With respect to large-scale deployment of new energy infrastructure, examination of historical patterns of deployment of a new fuel provides a temporal measure of the inertia in America's fuel system. This can be taken as a guide to what may be expected for future rates of change in our energy system. Let's take as this guide the time it takes for a new fuel to increase its share of the total U.S. energy supply from 10% (the point at which the fuel resource and fueling infrastructure has penetrated the supply market) to 50% (the point at which the fuel and infrastructure is the major portion of the total supply).

For coal (replacing wood as America's first fuel resource) this period was 35 years (1850 to 1885); for petroleum and natural gas, also 35 years (1910 to 1945). These fuel resource substitution periods [6] are also consistent with the above estimates of 30 to 40 years for average energy facility lifetimes.

For a completely new fuel concept, the additional time required for up-front R&D could add decades, extending the period for widespread implementation of new energy technology to 50 years or more. For our energy supply and infrastructure, the implications of change occurring incrementally over a period of decades are profound:

- New technologies cannot provide immediate solutions for a serious fuel or energy crisis.
- It takes decades to respond to environmental concerns such as global climate change with new technology. Even if we respond immediately to an identified environmental threat such as climate change, deployment of technology will take decades to have an impact.
- The concept of a non-carbon based hydrogen energy economy is a laudable goal that we should vigorously pursue. However, many hydrogen technologies are in early stages of development [7], and compared to fossil fuels that supply 85% of U.S. energy needs [1], there is little infrastructure for hydrogen. Hydrogen will not be a major contributor (say 50% of supply) to the U.S. energy system for nearly half a century.
- To be effective, development of energy policy must take into account that change in the energy system must occur incrementally over decades.

It is clear that because of the long time scales involved in incrementally changing our energy system, implementation of new technologies must be vigorously pursued and supported or they will not begin to make significant contribution to energy supply for many decades.

3. Stable long-term energy policies are needed. Policy is what is done through government to solve public problems or resolve public issues. Since the energy crisis of the 1970s, there have been myriad energy policies enacted by Congress. The difficulty with current and past energy policy is that it hasn't provided stable long-term solutions to U.S. energy problems. Development of energy policy must recognize and be consistent with the time scale and incremental evolution of the U.S. energy system, as noted above. To be effective, energy policy must continuously evolve over decades in response to changing U.S. energy requirements and new technology.

The instability of U.S. energy policy development is evident from examination of the intense period of U.S. energy policy development that followed the OPEC oil embargo of 1973. Three administrations--Nixon, Ford, and Carter--several Congresses, and a multitude of energy and environmental interest groups struggled to develop energy policies that would solve the problem created by the paradigm shift of energy abundance to energy scarcity. By 1980 basic long-range energy policies had been hammered out. America had the beginnings of a national consensus on energy issues.

The policy system started working. The policies created incentives for energy conservation and efficiency, for producing more oil and gas, and for producing clean coal technologies. Policies also gave emphasis to environmental concerns and placed a moratorium on new nuclear power plants. And, R&D programs were initiated to develop and provide alternative energy options. The conservation and efficiency policy efforts, especially the mandated improved mileage for automobiles (CAFE standards), caused a drop in demand for oil in the 1980s, helping to create the seemingly abundant, low-cost energy we've enjoyed for nearly two decades.

So what happened? Why are we facing many of the same 1970s energy problems today? One reason is that the energy policy pendulum swung in the opposite direction--away from policy-guided to market-guided decisions. In 1981 President Reagan's administration, espousing a "free market" philosophy, with broad

political and public support, began a process of dismantling the policy system that had evolved over a decade. The Reagan administration also drastically reduced R&D budgets for new energy technology. The feeling during the 1980s and 90s was that energy is plentiful and cheap, so why do we need energy policy? Let the market deal with the supply and demand issues. Today America is experiencing some of the consequences of the dismantling of the energy policy system of the 1970s, and will have to revisit many of the same issues to develop new policies to deal with them.

But what's the status of U.S. energy policy today? In an interview for *Running on Empty*, Senator Jeff Bingaman, Ranking Member of the Senate Energy and Natural Resources Committee, summarized the policy situation as Congress wrestled with energy policy in 2001 [8]:

"The truth is we've got lots of energy policies sitting around Washington and, you know, you could look at virtually any two-year period for the last 20 years and find at least one energy policy that has been developed and put out there for everyone to consider.

"The problem is we haven't had a set of policies that we could pursue with any kind of consistency and commitment over a long enough period of time to make any difference. And so that's what we really are challenged with doing this year [2001], is to come up with a set of policies that we will actually commit the country to pursuing for a period of time and that, of course, are enlightened enough to move us in the right direction."

The energy policy efforts of the 1970s has taught us that policy must be made incrementally, especially for something as big and complex as our energy system. We have to approach energy policy by recognizing our strengths. We have to understand the institutional and political landscape as it is, then consistently move in small steps toward broadly defined goals.

4. Continuous public involvement and support is essential. Politicians are sensitive to the views of the public. After all, they owe their jobs to the electorate. Public concerns become political concerns addressed by policy. In our interview of James Schlesinger [9], the first U.S. Secretary of Energy, he noted connection between public support and policy:

"There is a strong degree of public support for cleaning up the environment. In the environmental area we are prepared to spend more on automobiles, we are prepared to force utilities to clean up their emissions and you have a willingness to clean up the air from pollutants. In the energy area dedication comes and goes."

"This is a democratic country and the public wants low energy prices, and if you want to move in the direction of diminishing dependency on foreign sources of supply, or move in the direction of government support for additional infrastructure, that tends to add to energy prices. The public has wanted to keep energy prices [low] and in a democracy the politicians are very sensitive to that. In the abstract, people like myself may say that energy policy should have been far more ambitious in this respect that we've had since the early 1980s but it has not been because there's been no public demand, and those who have worried about the problem have tended not to earn support at the election booth."

Clearly public interest waxes when there are energy shortages or energy and fuel prices rise, and wanes when supplies are plentiful and prices low. How can public interest be maintained through the ups and downs of energy prices, and how can the public be brought more directly into the policy making process? Here are a couple of thoughts.

Public outreach. For all our dependency on energy, the public has little understanding of the technology and systems that deliver power to our fingertips, and little knowledge of technological developments that can provide solutions to current energy problems and associated environmental concerns. The nation's political,

educational, and media systems must redouble efforts to provide the knowledge and skills necessary for Americans to think critically about the costs and benefits of energy technology development and use. And, scientists and engineers must share their knowledge with the public, in terms that can be understood. This needs to be done continuously, not just in times of energy crisis.

Energy town hall meetings. Public participation in planning and developing recommendations for long-term national energy policy could be implemented through a consensus-driven town hall approach, such as the Twenty-ninth Town Hall on New Mexico's Energy, Economics and Environment [10] conducted in 2002 by New Mexico First, a non-profit, non-partisan public policy organization. The New Mexico First Town Hall process reflects the vision of New Mexico First's founders, United States Senators Pete V. Domenici (R-NM) and Jeff Bingaman (D-NM), who wanted a vehicle for policy makers to hear from the citizens of New Mexico regarding policy recommendations.

Recommendations resulting from the town halls carry weight with New Mexico's legislators, cabinet secretaries, and the executive branch for two reasons. Town hall participants represent New Mexico's diverse cultural, geographic, economic and political population, and the recommendations result from a consensus-driven process. The recommendations of the Twenty-ninth Town Hall on New Mexico's Energy, Economics and Environment have found their way into recent New Mexico energy legislation. A similar process, with a series of nationwide town halls, could be used to bring the public into the national energy policymaking process.

A Road to Fuels of the Future.

Why a road is needed. Today, America has a challenging opportunity to build a road to fuels of the future that will supply the needs of our transportation system and avert an imminent fuel crisis. The opportunity results from U.S. dependence on imported petroleum and a gap that will soon form between the supply and demand curves for petroleum as global petroleum demand increases by 50% over the next two decades, and worldwide petroleum production peaks within this decade [11]. Our interview [12] of Dexter Sutterfield, Division Director of Petroleum Technology Management for the DOE's National Petroleum Technology Office underscores the urgency of the petroleum situation:

"Our [worldwide] consumption of crude oil right now [2001], is about 77 million barrels a day. By 2020 we expect that consumption to be about 117 million barrels a day. And the biggest increase is in that use worldwide will be in developing countries like China, Africa, South America, places that are developing and also that have a lot of the resource, and as such, we will be hard-pressed in the United States because we will need to be more efficient because they're going to use their own resources and so running on empty is a real term here. When there's a demand for us and demand for the country where the crude oil's being produced, I have an idea that we will be the ones that wind up on empty."

Policy enables filling the fuel supply/demand gap. How can America fill the gap between supply and demand for transportation fuels as this gap forms, then widens? Technology options compatible with our current fuel supply infrastructure are available. What will it take to deploy these options? The lessons of the past tell us that we will need to:

- Deploy the options incrementally over a period of decades.
- Have stable long-term policy to support deployment of the options.
- Have continuous public involvement and support.

To fill the gap U.S. energy policies will have to tackle both the supply and demand curves to bring them into alignment to eliminate the gap. And the public will have to encourage and be supportive of development of those policies.

As the supply-demand gap forms, U.S. transportation fuel supply can be incrementally augmented by liquid fuels produced from coal and biomass. With respect to demand, the fuel efficiency of vehicles must be dramatically improved with technology such as hybrid electric vehicles. Policy in the areas of augmenting supply (for example an alternative fuel standard similar to the renewable electricity standard considered by Congress) and decreasing demand (a return to improved CAFE standards) will be needed to insure that once we start down the road to fuels of the future, we stay on course to complete the journey—that in the long term, we protect the technologies we deploy.

In our interview of James Schlesinger [9], he underscored the need to protect investment in new technology: "...we must recognize that even when we have vast technological improvements that those technologies require long lived, costly investments and those who we wish to induce to make those investments must feel that they have some protection against what is still a very powerful set of oligopolists in OPEC. That is something that we have learned with regard to new technologies. That new technologies must be protected if they are to be introduced en masse."

A modest investment with large returns. Let's make a simple estimate of the investment that would be required for one scenario, that of filling the supply-demand gap with coal-derived transportation fuels. (An equivalent investment must also be made in biofuel alternatives, but for lack of cost data will not be examined here.) Suppose the U.S. government makes an investment equal to just 2% of the \$500 billion annually invested worldwide for energy supply systems, and commits \$10 billion/year for ten years to develop alternative fuel infrastructure. Further, suppose government shares half the cost of constructing the new infrastructure with American companies, making the combined investment of \$20 billion/year. Assumptions are: a construction cost of \$1 billion to build a plant producing 30,000 barrel/day of gasoline and diesel and 700 Mw of electricity, and a plant construction time of about five years. Within fifteen years, the investment could add an additional six million barrels a day of gasoline and diesel from coal (or 60% of current imports), and 140,000 megawatts of electricity (20% of current supply).

Compared to the other government programs, the cost is modest. The annual cost of \$20 billion/year would amount to only 0.17% of U.S. gross domestic product (\$11.4 trillion for 2004 [13]). The total government and private investment for coal co-production energy infrastructure over ten years would be \$200 billion. When compared to the estimated ten-year defense budget of \$3.7 trillion, it's a real bargain.

Investment in our energy infrastructure will yield payoffs equal to one of the best long-term government investments America ever made--the Interstate Highway System. That program involved every state, hired millions of Americans, positioned the U.S. for improved international competitiveness, enriched the life of virtually every American, and returned six dollars for every dollar of the \$400 billion it cost. Investment in our energy infrastructure will surely do the same.

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